



**PERFLUORINATED COMPOUNDS, BISHENOL A AND ACETAMINOPHEN IN  
SELECTED WASTE WATER TREATMENT PLANTS IN AND AROUND CAPE  
TOWN, SOUTH AFRICA.**

**by**

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Date

## ABSTRACT

The release of wastewater to the aquatic environment is most likely to introduce some trace levels of organic contaminants, some of which may be toxic, carcinogenic, or endocrine disruptors, as well as, persistent in the environment. Additionally, increasing contamination of surface waters by wastewater effluents has made water treatment processes more challenging and expensive. The presence of these pollutants in the receiving water body may have negative effects on aquatic species and often pose potential human health risks through the reuse of treated wastewater for drinking purposes and other household use. In countries like South Africa, Namibia, USA, Singapore and Australia, water agencies are intensifying wastewater reclamation/wastewater reuse as part of their water resource agenda: in order to meet the demands of the growing populations. Nowadays, water reuse is generally considered as a viable method of water supply management.

This study focused on the identification of the occurrence, quantification of emerging contaminants and evaluation of removal efficiency in wastewater treatment processes of three classes of emerging contaminants (ECs) in wastewater: 1) six types of perfluorinated compounds (PFCs), namely; perfluorooctanoic acid (PFOA), Perfluorooctane sulphonate (PFOS), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUDA); 2) bisphenol A (BPA); and 3) Acetaminophen (ACP). These contaminants were identified and quantified in four wastewater treatment plants in the Western Cape. These treatment plants include three WWTPs in Cape Town, namely: Bellville WWTP, Scottsdale WWTP and Zandvliet WWTP and one WWTP in the central Karoo (Beaufort West wastewater reclamation plant).

Water samples (wastewater at different treatment stages) used in this study were collected through the period of February to July 2015. Samples were collected in 2 L prewashed amber screw capped glass bottles. Analysis was performed in three sample batches for each treatment stage of the treatment plants, and the extraction method used was based on solid phase extraction (SPE). An analytical method using an Ultra performance liquid chromatography/quadrupole mass spectrometer (UPLC/MS/MS) was developed and validated for the analysis of the contaminants. The UPLC separation was performed on a ACQUITY UPLC™ BEH C18 1.7 µm column (2.1 mm ×100 mm) with an ACQUITY BEH C18 1.7 µm VanGuard™ precolumn (2.1 mm×5 mm) with mobile phases A and B that consisted of a mixture of 2mM ammonium acetate in Milli-Q water and methanol respectively. The column temperature was set to 50°C. Triple quadrupole mass spectrometry

was used for the qualitative and quantitative analysis of the UPLC/MS analysis. The method's limit of detection and limit of quantification were in the range of 0.014 – 0.036 ng/L and 0.0470 – 0.686 ng/L respectively and recoveries obtained for Oasis HLB cartridges range were between 82.5 – 102% in ultrapure water and 79 – 101.1% in wastewater.

The wastewater samples had up to 90 % occurrence of the studied analytes. Bisphenol A was the most observed analyte with the highest mean concentration at  $210 \pm 6.52$   $\mu\text{g/L}$  in Beaufort West WWTP. PFOA was the most observed PFCs while PFOS was the least detected. PFOS were not found at all in the samples from Beaufort West, Zandvliet, and was only detected in Scottsdale WWTP. In addition, higher effluent concentrations of some PFCs such as PFOA, PFNA and PFOS were observed in some treatment plants which might be because of desorption of PFCs from solids, matrix interference and degradation of PFCs precursors within the treatment plants. The maximum mean concentration of PFCs found in the samples were as follows: 48.53 ng/L of PFHPA in Zandvliet influent; 13.10 ng/L of PFOA in Zandvliet influent; 18.8 ng/L of PFNA in Beaufort West influent; 10.24 ng/L of PFOS in Bellville effluent; 6.21 ng/L of PFDA in Beaufort West influent and 4.22 ng/L of PFUnDA in Scottsdale. The average concentration of acetaminophen ranged from 27.96 – 175  $\mu\text{g/L}$  and ND – 5.23  $\mu\text{g/L}$  in influent and effluent respectively. The wastewater treatment processes reduced the influent concentrations of acetaminophen, bisphenol A and total PFCs by 95.6 – 100 %, 86.5 – 99.7 and 54.33 – 73.65% respectively. Higher removal was observed on plants with tertiary treatment technology compared to plants with only secondary treatment processes and greater percentage removal was found with plant (Beaufort West plant) with additional advanced oxidation treatments in the treatment train when compared in terms of the concentrations of the influent and effluent of all the studied plants.

The physicochemical parameters of the influent and effluent of the treatment plants were also studied. Samples were analysed based on the standard methods of water and wastewater quality. The result of the physicochemical parameters was discussed based on the South African and World Health Organization guidelines limit in both drinking water and wastewater. The observed level of pH, TDS, and EC in the final effluents of all the treatment plants were within the South African guideline and the World Health Organization limit recommended for effluent discharge. The TOC in effluents of Bellville and Zandvliet WWTPs exceeded the SA guideline. The COD in effluents from Zandvliet WWTP exceeded the SA guideline but the effluent COD of all the studied treatment are within the  $\leq 1000\text{mg/L}$  World Health Organization limit in wastewater effluents. However, the nitrite/nitrate levels

of all the wastewater treatment plant effluents exceeded the maximum allowable limit (12 mg/L) set by South African and World Health Organization for effluent discharge.

In conclusion, the generated data and findings of the research study will assist in understanding the efficiency of wastewater treatment methods used in the WWTPs in the removal of the studied ECs. However, the presence of the analytes in the final effluents requires further monitoring of their presence in the receiving water bodies and their effects on aquatic plants and animals. The long-term effects of the contaminants on humans that consume this water (especially the Beaufort West water reclamation plant) should also be investigated. Furthermore, the South African municipalities and the Department of Water Sanitation must implement guidelines and maximum allowable limits for emerging contaminants in wastewater effluent discharge and municipal drinking water.

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## **DEDICATION**

This thesis is dedicated to my late father, Mr Adeleye Abel Oluwasanmi. May his gentle soul rest in perfect peace. Amen

## LIST OF OUTPUTS

The following outputs are contributions by the student to scientific knowledge and development:

### **Oral presentation:**

- Detection and quantification of selected emerging contaminants in re-use water. Presented at the WISA Water Reuse Symposium, Johannesburg, South Africa. 27-29 September 2015.
- Research on perfluorinated compounds in wastewater for re-use. Presented at Water Research Commission Workshop, Ruslamere Conference Center, Langeberg, Durbanville, Cape Town, South Africa. 11 March 2016.

### **Postal presentations:**

- Analysis of acetaminophen wastewater treatment plants in and around Cape Town, South Africa. Presented at the 7th SETAC Africa Conference, Langebaan, South Africa. 5-8 October 2015
- Analysis of perfluorinated compounds in wastewater treatment plants in and around Cape Town, South Africa. Presented at the 4th YWP ZA Biennial and 1st African YWP Conference – WISA, Pretoria, South Africa, 16-18.

### **Report:**

WRC Final report (Project No K5/2369) Titled Emerging Contaminants in Wastewater Treated for Direct Potable Re-use: The Human Health Risk Priorities in South Africa

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## **GLOSSARY**

<b>AOP</b>	Advance Oxidation Process
<b>BOD</b>	Biochemical Oxygen Demand
<b>BPA</b>	Bisphenol A
<b>DDT</b>	Dichlorodiphenyltrichloroethane
<b>DWA/DWAF</b>	Department of Water Affairs/Department of Water Affairs and Forestry
<b>ECs</b>	Emerging contaminants
<b>LC</b>	Liquid chromatography
<b>LOD</b>	Limit Of Detection
<b>LOQ</b>	Limit of quantification
<b>MS</b>	Mass spectroscopy
<b>PAHs</b>	Polycyclic Aromatic Hydrocarbons
<b>PBDEs</b>	Polybrominated Biphenyl ether
<b>PCBs</b>	Polychlorinated bisphenyls
<b>PFASs</b>	Perfluoroalkyl sulfonates
<b>PFCAs</b>	Perfluorocarboxylic Acids
<b>PFCs</b>	Perfluorinated Compounds
<b>PFCs</b>	Perfluorinted Compounds
<b>PFDA</b>	Perfluorodecanoic acid
<b>PFHpA</b>	Perfluoroheptanoic acid
<b>PFHPA</b>	Perfluoroheptanoic acid
<b>PFNA</b>	Perfluorononanoic acid

<b>PFOA</b>	Perfluorooctanoic acid
<b>PFOS</b>	Perfluorooctane Sulfonate
<b>PFUnDA</b>	Perfluoroundecanoic acid
<b>POSF</b>	Perfluorooctane Sulfonyl fluoride
<b>RO</b>	Reverse Osmosis
<b>RP HPLC</b>	Reversed Phase High Performance Liquid Chromatography
<b>SABS/SANS</b>	South African Bureau of Standards/South African National Standards
<b>SPE</b>	Solid phase extraction
<b>TDS</b>	Total Dissolved Solids
<b>TOC</b>	Total Organic Compounds
<b>TSS</b>	Total Suspended Solid
<b>USEPA</b>	United State Environmental Protection Agency
<b>USEPA</b>	United States Environmental Protection Agency
<b>WHO</b>	World Health Organisation
<b>WRC</b>	Water Research Commission
<b>WWTP</b>	Wastewater Treatment Plant

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Water constitutes an integral component of human survival. For sustainability, there is a need to protect this resource against external threats. In addition, the distribution of safe water, protection of the integrity of the available water resources, as well as, the protection of human health and the ecosystems have been important environmental issues for many years and will be significant in years to come. It is not an overstatement that the global demand for clean water, both in quality and in quantity, is currently greater than the supply. The section 24 of the 1996 South African environmental Constitution states that everyone has the right to have access to an environment that is not harmful to his or her health or well-being, and this includes a constant supply of clean and safe water. However, the growing human population, industrialization, global climate change, accelerated agricultural practices have contributed a lots to non-availability of fresh drinking water to humans. South Africa has been classified as a water-stressed country because of the experienced low annual rainfall (average of 450 mm) when compared to the global annual rainfall of 860 mm (Benhin, 2006).

Furthermore, economic development and population growth in South Africa have contributed to increase in water demand. The production of valuable consumer products is also an indicator of this growth. However, extensive use of organic compounds in the modern society and their release via wastewater has resulted in environmental contamination of both source and drinking water. Hence, recovering clean water from wastewater is now recognized as one of the limited alternatives to supplement the shortage of clean water. Nonetheless, these wastewaters often contain chemicals of different components, varying over time and places. As wastewater is reticulated into various treatment plants, the functionality and efficiency of the treatment plants are not considered for treatment of most synthetically produced organic compounds, (especially the emerging contaminants). Consequently, water and sewage treatment plants progressively function under pressure. There is a growing concern about water quality and the impact of untreated or poorly treated wastewater that are released into the environment of South Africa (Mema, 2010).

Over decades, the presence of non-polar toxic chemicals in water has been a subject of major scientific interest in the outline of water monitoring programs. Therefore, great attention has been given to contaminants, such as, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals. Thus, there have been guidelines provided on the concentrations of these chemicals in order to protect water quality (Hadjibiros et al., 2011; Kalantzi & Siskos, 2011). Recently, the presence of emerging contaminants (ECs) has been recognised to cause significant environmental problems with different adverse health effects on humans and aquatic life. This group of pollutants is composed of products used in vast quantities in everyday life, including human and veterinary pharmaceuticals, plasticizers, surfactants and surfactant residues, personal care products, phthalates, nanoparticles, and different industrial chemicals (Petrović et al., 2003). Emerging contaminants comprise of toxic chemicals, endocrine disruption compounds and persistent organic pollutants. According to Smital. (2008), ECs has been defined as synthetic chemicals, which have been present in the environment for a long period, but only lately detected by modern instrumental methods or newly synthesized chemicals recently been detected upon release in the environment. The United State Environmental Protection Agency (USEPA) has defined ECs as unregulated compounds, newly identified/studied in water sources that may have a negative impact on the environment (Deblonde et al., 2011). Thus, this research is to identify and quantify some selected emerging contaminants in waste water treatment plants and to determine the performance of the treatment processes on the removal of the contaminants.

## **1.2 Significance of the research**

Several emerging contaminants have been identified in the wastewater treatment plant (WWTP) influents and effluents (Bedner & MacCrehan, 2006; Arvanitia, et al., 2012; Anumol, et al., 2013). These substances are released into the aquatic environment through WWTP effluents. The occurrence of pollutants limits wastewater re-use, particularly when the pollutants are not effectively removed by treatment processes and are harmful to humans and aquatic plants and animals. Greater knowledge of treatment efficiency on the removal of these substances from the point source will protect both humans and aquatic habitats from these adverse effects. The results of the evaluation of most ECs on their possible toxic effects on both the aquatic ecosystem and human health have classified them as possible carcinogens. Recently, the USEPA, researchers have considered it crucial to monitor the environmental sources and exposure pathways of ECs in the environment globally. Results on several studies on perfluorinated compounds (PFCs), bisphenol A and acetaminophen

show their extensive occurrence in wastewater, drinking water and the aquatic environment. In South Africa, there is limited information on their presence in wastewater inflow, effluents and receiving waters as well as the efficiency of wastewater/water treatment plants to remove these compounds. Therefore, it is essential to have a precise knowledge of the chemical pathways of these studied analytes, such as the physicochemical forms in which the contaminants exist, the concentrations at which they are present in WWTPs, and to predict their release rate. The generated data could however assist in understanding the efficiency of wastewater treatment methods used in the WWTPs in the removal of the studied ECs.

### **1.3 Statement of research**

Most toxic organic compounds are present in different chemical forms in air, water, soil, sediments, biota etc. PFCs, bisphenol A and acetaminophen are no exception to this fact. They can be released into the environment from manufacturing processes or via the use of products containing these compounds. The subsequent release as well as land draining of these toxic compounds into the aquatic systems by industrial and domestic activities may pose serious problems to water quality and aquatic life. Hence, there is a need to monitor their removal during wastewater treatment processes. Unfortunately, due to the resistance of several ECs to oxidation, conventional methods have been proven inefficient for their total removal in wastewater (Radjenovic et al., 2007; Becker et al., 2008). Therefore, there is a need for the development of effective treatment methods for the removal of these compounds from wastewater treatment plants. Furthermore, because many of these compounds are not regulated in wastewater effluents or in drinking water, and can impact aquatic environment even at trace concentrations, it is imperative to monitor these contaminants in wastewater treatment plants until there is adequate knowledge of their presence, fate and behaviour as well as their toxicity to humans. To achieve this, there is a need to develop analytical techniques for the chemical separation and subsequent analysis for effective monitoring of these compounds.

### **1.4 Aims and objectives**

The main aim of this study was to understand the occurrence of PFCs, bisphenol A, and acetaminophen with attention on the removal efficiency of different stages of water treatment processes. This aim was achieved by investigating the level of occurrence of these

contaminants in wastewater treatment plants in and around Cape Town. Hence, the main aim was achieved by pursuing the following objectives:

- To determine the physico-chemical characteristics of the wastewater.
- To validate an analytical method for the simultaneous determination of selected PFCs, bisphenol A and acetaminophen in wastewater samples.
- To identify and quantify the concentration of selected PFCs, Bisphenol A and Acetaminophen in wastewater treatment plants influents and effluents
- To establish the removal efficiency of PFCs, bisphenol A and acetaminophen during wastewater treatment processes

### **1.5 Research Questions**

The following research questions are addressed

- Are PFCs, bisphenol A and acetaminophen present in wastewater?
- If present, in what concentration?
- Are the existing treatment methods suitable to completely remove these compounds from the wastewater?
- What form of treatment mostly removes these compounds

### **1.6 Delineation of research**

This research focuses on understanding the efficiency of treatment processes at four Western Cape WWTPs in the removal of some selected contaminants (PFCs, bisphenol A and acetaminophen). Although water matrices may contain several other pollutants, only six selected PFCs, bisphenol A, acetaminophen were the target compounds in this study due to their wide use, occurrence in the environment, and time frame to complete research. Furthermore, this study will not cover the following

- Analysis of PFCs such as the fluorotelomer alcohols, sulfonamides, fluoropolymers and all other PFC precursors
- Effects of seasonal variation on the presence of the studied contaminants in the wastewater treatment plants.
- Studies on acetaminophen and bisphenol A metabolites and chlorinated derivatives
- Studies of health effects of the contaminants
- Studies on wastewater treatment plants outside Western Cape.

## 1.7 Outline of chapters

The overall aim of this study is to understand the occurrence of PFCs, bisphenol A, and acetaminophen with attention on the removal efficiency of different treatment processes. This aim will be achieved by quantifying the concentrations of these contaminants in wastewater treatment plants in and around Cape Town, South Africa. This thesis is sectioned into the following chapters in accordance with the guidelines provided by Cape Peninsula University of Technology for thesis write-up:

**Chapter one:** The introductory chapter provides background on the importance of water, and of wastewater treatment on the removal emerging contaminants for water reuse. It presents the significance, statement, and aim of the research. It also highlights research questions, which will be addressed by the study, the research objectives and concisely delineates research topics that were not covered by the study.

**Chapter 2:** The literature review chapter presents the characterisation, generation and sources of wastewater as well as situation of water use and the implemented quality control in South Africa. Description of basic wastewater treatment processes is presented in this chapter as well as information on the studied emerging contaminants and their properties. This chapter also covers the production, sources in the environment, routes of human exposure, and their toxic effects. The chapter provides a thorough review of the global occurrence of PFCs, bisphenol A, acetaminophen and the reported efficiency of treatments on these compounds. Physicochemical parameters of water and a review of analytical techniques for the identification and quantification of the studied ECs are also discussed.

**Chapter 3:** The research methodology chapter provides detailed analytical techniques including materials and methods used in this study. Information on sampled treatment plants such as the available treatment processes in each treatment plant, sources of plant inflow, plant capacity, average population served, as well as sample collection procedures are discussed. Methods for determination of the sample physicochemical properties are also described.

**Chapter 4:** This chapter presents the results and discussion. The results of the level of occurrence of the studied ECs as well as the treatment of efficiencies of the available treatment technologies in the studied WWTPs are presented and discussed. Furthermore, the result of the physicochemical parameters of the WWTPs influents and effluents are presented and discussed.

**Chapter 5:** This chapter describes the overall discussions and conclusions of this study. It provides answers to the research questions highlighted in chapter one. It also lists recommendations for future studies.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

Water is a vital sanitation parameter as well as an economic factor. A good and healthy living requires constant, safe and clean water supplies. Unfortunately, this has not been accomplished equally worldwide. In South Africa the government implemented a “Strategic Framework for Water Services” to ensure basic water supply of at least 25 litres of improved drinking water to the citizens (DWAF, 2003). As creditable as this program might seem, one of its shortcomings is that increases in water supply will possibly lead to increased wastewater generation which might end up aggravating the already bad water situation in the country if proper attention is not given to the operational efficiency of the existing wastewater treatment plants (Odjadjare & Okoh, 2010). Reuse of treated wastewater effluents has been highlighted as a possible way to ensure continuous availability of water as well as a way to reduce the possible ecological risk posed by exposing organisms to anthropogenic contaminants. Conversely, the presence of chemicals and micro pollutants is a huge challenge faced by treatment plants. These contaminants limit the acceptability of treated wastewater for potable water reuse due to the reports of their adverse effect on humans. Studies have shown that the existing conventional treatments in South Africa are inadequate to treat wastewater prior to reuse or discharge (Morrison et al., 2001; Olujimi et al., 2013). The aquatic environment and drinking water sources can be polluted with chemicals, biological, microbial, and micro pollutants, upon discharge of wastewater treatment plant effluent into the environment. This can impact aquatic life which might sometimes cause changes in species composition, change in habitat and decrease in species biodiversity. There are also concerns about the qualities of reclaimed water which might contain some level of these contaminants. Water physicochemical parameters like pH, temperature, electrical conductivity (EC), nitrate, phosphate, total dissolved solid (TDS), total organic carbon (TOC), and carbon oxygen demand (COD) have been prescribed to improve biological and chemical quality within water treatment systems. Changes in the level of these parameters, indicates changes in the situation of the water system and this has a great effect on the quality of water for its beneficial use (Odjadjare & Okoh, 2010). Lately, application of new advanced treatment methods and advanced oxidation processes (AOPs) for water/wastewater treatment has been recognized and demonstrated to be effective in both degradation and total mineralization of organic pollutants. Choosing analytical techniques

that can detect and quantify these contaminants at trace level is one of the important tools needed to confirm water quality adequately and to understand the efficiency of treatment processes. This chapter therefore provides information on wastewater, the situation of water use and wastewater generation in South Africa, and physicochemical properties of water. A review on the selected emerging contaminants in this study is provided. For example, their manufacture, uses, sources to the environment, toxicity as well as the previous research done on these contaminants are discussed. Analytical techniques for the detection and identification of these contaminants in water matrices are also reviewed.

## **2.2 Wastewater**

Water is said to become a waste when organic pollutants, microorganisms and bacteria, discharge from industries, or introduction of compounds that might change its original quality have adversely contaminated it. Wastewater sources include, industrial, municipal, storm water, surface runoff and agriculture activities (El Saliby, 2012). Municipal wastewater (Figure 1.1a) refers to the liquid waste contaminated with washing water (personal, clothes, floors, dishes), urine, faeces and any other substances discharged by domestic residences and/or commercial properties. Industrial wastewater (Figure 1.1b) comprises of different dissolved chemicals and sometimes colours from various industrial activities such as food processing, iron and steel industry, mines and quarries, textile factories, and so on. Agricultural effluents comprise of microorganisms, high concentration of organics from animal and vegetable sources and various chemicals used for pest and disease control. Both treated and untreated industrial and municipal wastewaters are frequently released into aquatic environments. It has been confirmed that wastewater contains suspended solids and macro-solids, inorganic matter (such as; minerals, metalloids, trace-metals, oil and grease), organic matter, nutrients (e.g. nitrogen and phosphorus), microorganisms, pathogenic and non-pathogenic bacteria, emulsions, toxins, gases, and pharmaceuticals (El Saliby, 2012). Generally, the composition of wastewater depends on the source and activities involved.

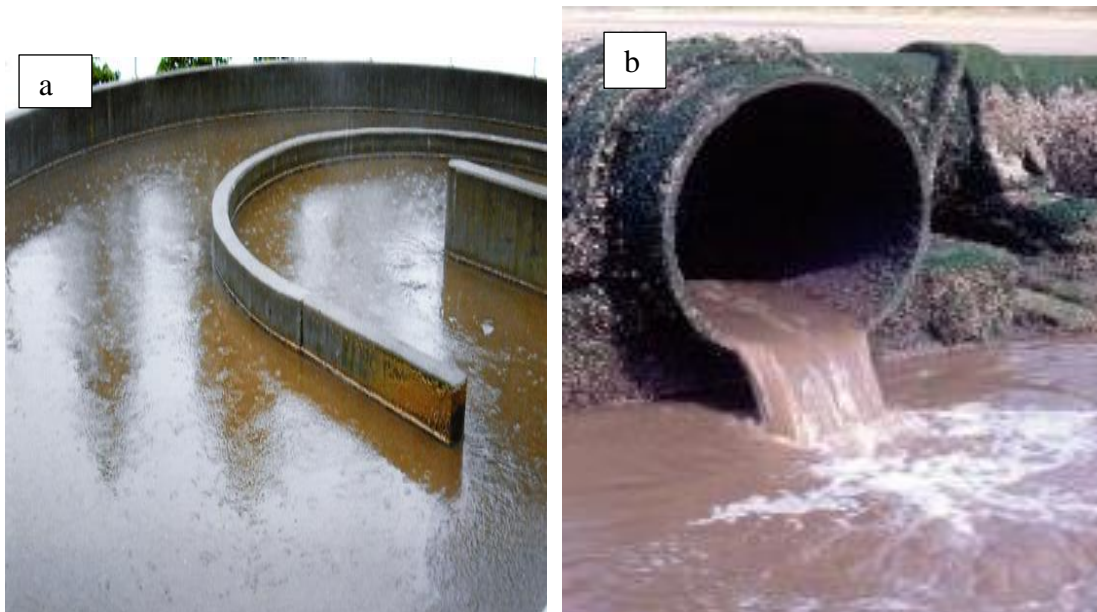


Figure 1.1: Municipal wastewater treatment plant at Beaufort West (a) and industrial wastewater discharged through a pipe to the environment (b)

There has been concern over the presence of organic contaminants in aquatic environments, which function as water sources for potable water treatment plants. This is due to the potential negative environmental and possible human health effects from exposure using contaminated water, reclaimed/recycled for both potable and non-potable purposes. Reclaimed/recycled water is a wastewater that has been treated to eliminate solids and some other contaminants, and then reused for different purposes. The recycling and recharging is typically done by using the treated wastewater for selected municipal sustainable agricultural irrigation practises (Khamis et al., 2011) .

Reclaimed water is intended to be solely used for non-potable purposes in most countries. Due to fresh water scarcity, the use of reclaimed water for potable water supply, for agricultural and industrial purposes has been one of the basic topics in water resource management. Therefore, studies of the effects and fate of organic contaminants in sewage water discharged in the environment have been given more attention. Contaminants may either be partially retained in the sludge or transformed from the parent compound to a more hydrophilic and persistent form (Khamis et al., 2011). These compounds pass through the wastewater treatment process without being completely removed. Consequently, they end up in receiving water bodies (Radjenovic et al., 2007; Bolonga et al., 2009). To guarantee that treated water is free from any substance that might adversely affect human health and the environment, all contaminants present should be identified to ensure that they are completely removed. Therefore, suitable detection and treatment methods need to be put in place.

## **2.2.1 Physico-Chemical Characterization of Wastewater**

Three main constituents generally describe chemical characterisation of municipal wastewater: the organic nutrients, phosphorus and nitrogenous compounds. The organic nutrients comprise of carbohydrates, fats and proteins. Phosphorus is present as phosphates from domestic waste, while nitrogen is primarily present as ammonia. Physical characterisation of wastewater involves separation into dissolved, suspended and settleable constituents by settling and filtration. Municipal wastewater also has other constituents like grit, anions and cations, living biomass and anthropogenic pollutants (Ivarsson & Olander, 2011) such as emerging contaminants. All these constituents have to be considered in the wastewater treatment process. Therefore, there is a need for wastewater characterization.

### **2.1.1.1 Chemical oxygen demand (COD)**

During wastewater treatment (in the activated sludge processes) bacteria is responsible for the degradation of organic matter. Chemical oxygen demand (COD) is usually one of the parameters mostly used to quantify the degree of efficiency removal of organic matter in wastewater. COD is defined as the quantity of a substance expressed in terms of comparable oxygen, required to oxidize the sample under monitored conditions (Akan et al., 2008). Mekibib. (2011) explains that COD measures the amount of oxygen needed to totally and chemically oxidise organic substances and mineral compounds to inorganic end products. The greater the difference between the amounts of COD in the wastewater influent and the final effluent, the greater the removal of organic matter and thus, the better the wastewater treatment efficiency (Eaton et al., 2005). Consequently, COD remains an important and fast quantifiable parameter for the assessment of the organic substance content of water expressed in milligrams of oxygen per litre (mg/L).

### **2.1.1.2 Measurement of COD**

Although most research papers have stressed the importance of COD in water toxicity assessment, little information is available in the literature on the experimental technique used for the measurement of this parameter. Soresa. (2011) and Daniel, (2015) described a methodology for COD measurement and calculation using ferrous ammonium sulphate titrant (FAS)  $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  for standard solution preparation and the COD concentration is calculated using the formula shown in the Equation 1.

$$\text{COD (mg/L)} = \frac{[(\text{FAS}_b - \text{FAS}_s) * \text{M} * \text{Df}]}{V_s} \dots\dots\dots (1)$$

Where  $\text{FAS}_b$  = ferrous ammonium sulphate concentration (mg/L) used for blank

$\text{FAS}_s$  = ferrous ammonium sulphate concentration (mg/L) used for sample

M = molarity of FAS

Df = dilution factor (8000)

$V_s$  = sample volume used (mL)

COD can also be analysed spectrophotometrically according to the standard method described by EPA Method 410.4. This method was applied in this study and short description of the method is given in chapter 3.

### **2.1.1.3 Total organic carbon (TOC)**

Total Organic Carbon (TOC) is the total amount of carbon present in the organic compounds in an aqueous solution. Parameters such as, colloidal particles, suspended particulates, COD and biochemical oxygen demand (BOD) are all part of the TOC. In addition, it has been possible in some cases, to relate TOC to COD and BOD values in order to measure pollution characteristics (Metcalf & Eddy, 2003).

### **2.1.1.4 Total suspended solids (TSS)**

Total Suspended Solids, TSS, describes the amount of emitted suspended solids including, inorganic fillers, fibres, and pigments in the wastewater. At low TSS concentration, there is no specific environmental problem connected to their release. However, it is of utmost importance to separate as much TSS as possible because it can have negative effects on the biological treatment and the solids can cause clogging problems in pipes and pumps.

### **2.1.1.5 Temperature and pH**

Temperature is an important environmental characteristic. It influences the behavioural features of organisms as well as solubility of salts and gases in water. For example, an increase in temperature, phosphate and nitrates may result to an increase in algae and plant growth. The temperature and pH of wastewater can influence the performance of activated sludge systems. Measurement of this parameter is also very vital because most wastewater treatment systems contain biological processes that are temperature dependent. The higher the temperature in a wastewater treatment system, the faster the biological rates (specifically, the rate of nitrification and denitrification) and vice versa. Conversely, an

increase in the temperature of wastewater effluents may become an obstacle in the receiving water to fish mitigation thereby affection reproduction (Lokhande et al., 2011). pH is an indicator of acidity and alkalinity. This parameter is often used in the overall characterisation of water quality; it is of great importance in determining the quality of wastewater effluent. It is described as a measure of hydrogen ion activity and an indicator of hydrogen-ion level present in water. The hydrogen ion concentration is a significant quality parameter of wastewater since many of the chemical reactions in aquatic environment are influenced by any change in its value. Typically, the pH of natural waters ranges from 6.0 to 8.5. Waters with a high pH value greater than 10 are exceptional and can indicate contamination by strong bases like  $\text{Ca}(\text{OH})_2$  and  $\text{NaOH}$  (Lokhande et al., 2011). Generally, most biological reactions such as nitrification and denitrification influence the pH by taking up or releasing hydrogen ions which can affect the buffering (ability to resist pH change) ability of the wastewater (Mhlanga, 2010).

#### **2.1.1.6 Electrical conductivity**

Electrical conductivity (EC) is generally used to measure the total ionized constituents of water. EC is directly related to the sum of cations or anions and it is closely related to the total salt concentration. Sources of these salts include municipal storm water drainage, dissolved salts from domestic sewage, industrial effluent, or wastewater effluent releases (Mhlanga, 2010). High salt concentrations from domestic waste and waste brines can affect water re-use for different purposes. Studies have shown that salts such as  $\text{NaCl}$  and  $\text{K}_2\text{SO}_4$  are not readily removed by conventional water/wastewater-treatment plants (Morrison et al., 2001). The occurrence of high levels of salt in wastewater effluents can cause an increase in the salinity of the receiving water bodies and can have a negative ecological effect on aquatic organisms. Similarly, an extremely high salt concentration of above 1000 mg/l causes a brackish taste to water and is discouraged due to the possible health hazard (Morrison et al., 2001).

#### **2.2.2 Basics of Wastewater Treatment**

Wastewater contains high concentration of several pollutants. Consequently, treatment of wastewater is much more complicated than drinking water. The degradation or removal of the overall organic pollutants is a challenging process for wastewater treatment industries. Wastewater must be properly treated before it can be recycled or safely released into the

environment. Generally, sewage treatment involves two stages, namely primary, secondary and an optional tertiary treatment.

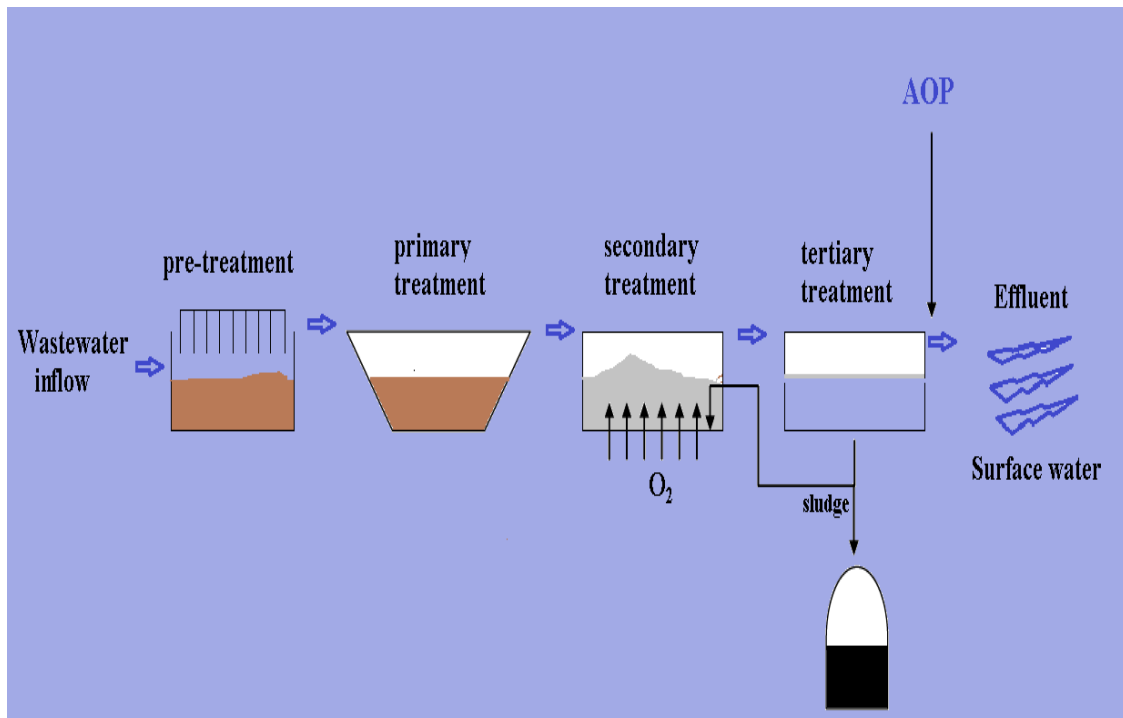


Figure 2.1: Schematic representation of a wastewater treatment plant.

AOP = Advanced Oxidation Process

### 2.1.2.1 Primary treatment

The primary treatment process is intended to remove gross, suspended and floating solids in the raw sewage. This is generally the first stage of wastewater treatment. Many advanced wastewater treatment plants in industrialized countries have started with primary treatment, and have then added other treatment stages as the wastewater load has grown and the need for thorough treatment has increased. Primary treatment process can be done mechanically. It includes screening to trap solid objects and sedimentation by gravity to remove suspended solids. This level is sometimes referred to as “mechanical treatment”, although chemicals are often used to accelerate the sedimentation process. The main purpose of primary treatment is to produce a homogeneous effluent, ready for biological treatment and a sludge that can be further treated. Primary treatment can reduce the BOD of the incoming wastewater by 20-30% and the total suspended solids by some 50-60%. It is ineffective for the removal of most persistent organic pollutants. Organic pollutants are removed predominantly by sorption on primary organic solid (sludge), as the dispersal of a compound into organic (lipophilic) layer is a major way of sorption. However, in a study by Stasinakis et al. (2013), it was found that primary treatment (sedimentation tank) partially removes

some endocrine disruptor compounds (EDCs). The removal efficiency ranges from 13% nonylphenol monoethoxylate to 43% bisphenol A (Stasinakis et al., 2013).

#### **2.1.2.2 Secondary treatment**

Secondary treatment processes remove up to 90% of the dissolved organic matter in wastewater. This is achieved using a biological treatment process. The biological treatment process can be categorized into aerobic, anaerobic and anoxic conditions. In the aerobic process, air is pumped into the aeration tank or the wastewater is vigorously agitated to allow transfer of oxygen. Microorganisms (specifically bacteria) consume the organic matter in the wastewater as food (for growth and reproduction) and so convert it to carbon dioxide, energy and water. Anaerobic process takes place in the absence of oxygen. Complete degradation of organic matter and the oxidation of inorganic matter are the best possible effects of the secondary treatment stage. Methods of treatment in a secondary plant include the well-known activated sludge process, constructed wetland structure, and membrane bioreactors. In a perfectly functioning secondary treatment plant, 85% BOD and suspended solids can be removed. For the current study, a brief description of the activated sludge process is provided.

##### **a) Activated Sludge**

The activated sludge plant is the most popular biological treatment process. It is a two-stage suspended growth biological treatment process aimed to remove organic material measured as BOD. The first stage of a basic activated sludge process is an aerated reactor where a mixed microbial population removes organic material. The second stage is a settling tank (clarifier) where the solids (activated sludge) settle and are removed from wastewater. Some portions of the activated sludge are returned to the aerated tank while some are disposed (removed from the process). Because activated sludge is returned to the tanks, their residence time in the system is higher than the hydraulic residence time. The average solids retention time is 5 to 10 days for conventional activated sludge. The mechanism of activated sludge process in ECs removal from wastewater is by biodegradation and/or adsorption to the solid material waste from the system, thus transfer of the pollutants from one phase (liquid) to another (solid)

#### **2.1.2.3 Tertiary treatment**

As previously discussed, not all organic contaminants are removed during primary and secondary treatment. Therefore, a tertiary/advanced treatment stage is needed to guarantee a

good water quality according to the national regulations before effluent is discharged into receiving water bodies. Tertiary treatment processes may include ion exchange, membrane filtration, activated carbon adsorption and advanced oxidation processes (El Saliby, 2012).

#### **a) Membrane Filtration**

In membrane filtration, treatment processes are characterized by the size of contaminants they remove. Membrane filtration processes include reverse osmosis, nano-, micro-, and ultrafiltration. Microfiltration and ultrafiltration remove suspended or colloidal particles through a sieving mechanism based on the size of the membrane pores relative to that of the particulate matter (solids and microorganisms). Reverse osmosis (RO) and nanofiltration membranes (NF) do not have definable pores. RO is a method commonly used for desalination by separating the water molecules and the ions through a membrane under pressure. The principle of osmosis is applied in this wastewater treatment technique. This method is also considered as a further treatment step to remove residual micro-pollutants from wastewater. Osmosis occurs when the molecules (specifically water) and their concentration gradient pass through a semi-permeable membrane. The semi-permeable membrane permits only water to pass through the membrane. Ions and larger molecules are not allowed through the membrane. The process of osmosis is thermodynamically favourable and will continue until equilibrium is attained. However, the process can be stopped and reversed by applying higher pressure (which must be greater than the osmotic pressure) on the concentrated side of the membrane. RO is energy intensive due to the high pressure required for the process. For compounds and particle removal efficiency, RO has been identified to be more efficient than UF (Ivarsson & Olander, 2011).

#### **b) Membrane Bioreactor**

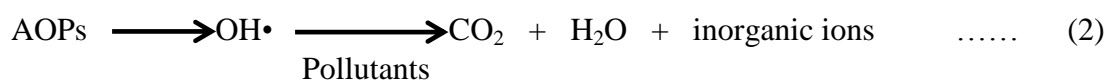
Membrane bioreactor (MBR) process is considered the most promising improvement in microbiological wastewater treatment. MBR process involves membrane filtration joined with biological treatment. The MBR solid/liquid membrane filtration takes place within either the bioreactor or externally recirculation. This is subject to a pressure drop via the membrane which is generated by either a fitted pump or a hydraulic head. Currently, social and economic reasons no longer limit the application of MBRs in municipal and industrial WWTPs and higher standards are set for wastewater treatment. This process may be important in both direct and indirect recycling of wastewaters, because of two properties:

- I. The low sludge production (approximately halved). Therefore, bacteria are forced to mineralize partially degradable organic chemicals; and

II. The long life of the sludge provides the bacteria more time to adapt to the treatment resistant chemicals (Gander et al., 2000).

**c) Advanced Oxidation Processes (AOPs)**

Since some organic micropollutants are not eliminated during the different stages of conventional wastewater treatment and some of them are highly persistent, a more effective treatment step is needed. Presently it is being debated which method would be the best to remove these substances and consequently there are a variety of requirements. AOPs are recommended when wastewater components have a high chemical stability and or low biodegradability. Furthermore, a chemical wastewater treatment with AOPs can achieve the total oxidation of pollutants to CO<sub>2</sub>, H<sub>2</sub>O and inorganic compounds as well as their transformation into more non-toxic products. AOPs use several reagent systems such as photochemical degradation processes (UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>), chemical oxidation processes (O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) and photocatalysis (photo - Fenton reactives, TiO<sub>2</sub>/UV) to produce hydroxyl radicals (OH•) as shown in Equation 2.



OH• are highly reactive, non-highly selective and they attack most organic molecules (Richard, 2013).

**d) Ultraviolet Radiation and Hydrogen Peroxide (UV/H<sub>2</sub>O<sub>2</sub>)**

The UV light is a radiation with a wavelength of 4 – 400 nm. It is invisible to the human eye. Typically, UV radiation is capable of inactivating pathogenic microorganisms by reducing their ability to replicate, thus, decreasing the risk of further infection. In addition, UV light has the ability to reduce organic micro pollutants by photolysis. The effect of UV light is very low in this regard, thus, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is included to combine photolysis with oxidation for micro pollutant degradation (Ivarsson & Olander, 2011). In the H<sub>2</sub>O<sub>2</sub>/UV process, formation of hydroxyl radicals is generated by the photolysis of ultraviolet radiation and the corresponding propagation reactions. In addition, photolysis of hydrogen peroxide occurs when UV radiation (*hν*) is used, as indicated in the equation below



During wastewater treatment, low-pressure mercury lamps (LP - Hg) with a wavelength of 253.7 nm are mostly used. It is essential that the substances to be removed in the water can absorb UV light in order to be oxidized by this radiation (Richard, 2013).

### **e) Chlorination**

Chlorination is a process used to inactivate pathogens. Typically, chlorination involves the disinfection with chlorine gas or concentrated hypochlorite liquid in drinking water treatment plants prior to distribution to customers. Chlorine is also used to disinfect wastewater, mostly before reuse. Prior to release to the environment (especially to surface water), chlorinated wastewater may be dechlorinated, to prevent negative effects to aquatic life. Furthermore, chlorine can transform organic substances through oxidation and chlorination. Nonetheless, the chlorine reaction with organic material can produce chloroform and some other potentially toxic disinfection by-products such as dichloromethylhydroxyfuranone, potassium bromate, bromodichloromethane (BDCM) and chloroform (Ivarsson & Olander, 2011)

## **2.3 Wastewater Generation, and Water Use and Quality Control Guidelines in South Africa**

In South Africa, water use is categorised into six groups, namely: urban (domestic, commercial, and public supplies), rural (domestic and stock caring requirements), power generation, mining and industry, afforestation and irrigation. Irrigation has been identified to make up 62% of the total water use. In the year 2000, the total water requirement ( $1.287 \times 10^6 \text{ m}^3/\text{a}$ ) was very close to the estimated available water resources (Eddy, 2011). Many of the country's municipalities and industrialized regions such as Cape Town, East London, Bloemfontein, Port Elizabeth, Johannesburg, Pietermaritzburg, Pretoria and Beaufort West are the most expected water stressed regions. Although different guidelines for the safety and cleanliness of water systems have already been established for water quality globally, the implementation of guidelines and regulations by the South African government under the Water Act of 1956 (Act 54 of 1956) is a bold step toward a sustainable water quality management. The treatment of effluent to acceptable standards in order to encourage good water quality and water reuse was mandated. It became clear that the demand for water is becoming greater than the available water resources and water recycling would have to play an important role in managing the country threatened water resources. Consequently, the directive that prohibited the release of effluents into the water bodies was consequently retracted. According to WRC and DWAF (1995), it was subsequently required that all effluents be released to the watercourse from which they are initially abstracted. The general standard was then implemented in Government Regulation of 1991 in accordance with the Water Act of 1956. In this regard, effluents discharged were

monitored solely by the quality of the effluent. These effluent standards, which were originally published in 1962, proved inadequate. Therefore, in 1980 and 1984, a more strict standard was introduced which place more strict standards on heavy metals, salts and phosphates. Lately, the quality control of drinking water works and wastewater treatment plants in South Africa is generally determined by physical and chemical parameters.

Submissions from convections such as the Stockholm, Rotterdam and Basel conventions indicated that there is a need to implement stringent legislation on the use and release of micro pollutants in the environment. Although South Africa is involved in some of these international conventions, it is obvious that there is no stringent legislation on the use and release of organic micro pollutants. The National Water Act for effluent discharge and wastewater re-use standards (DWAF 2010), and the South Africa National Standard (SAN 241) on drinking water quality management of 2005 and 2011 listed some guidelines for different parameters such as microbial, physical, organoleptic and chemical safety requirements with no mention of organic micro pollutants/ emerging contaminants such as PFCs, BPA and acetaminophen (SAN241, 2005). As mentioned above, these parameters are regulated by the National Water Act, which described the limit values permitted to discharge WWTP effluent into the aquatic environment taking into account the source of WWTP inflow In this study, other parameters apart from emerging contaminants are also determined. This includes COD (chemical oxygen demand), TOC (total organic carbon), and electrical conductivity. Furthermore, parameters describing substances with similar chemical properties such as total nitrogen and phosphate and characteristics such as total dissolved solid of the wastewater are also determined.

## **2.4 Emerging contaminants in the aquatic environment.**

### **2.4.1 Classification of Contaminants.**

There are different categories of environmental contaminants. Emerging contaminants are classified based on different criteria like their source, toxicity (human and ecotoxicity) environmental persistence and so on. Emerging contaminants can be classified into three groups:

Persistent organics: - this is one of the main groups of emerging contaminants. Recently this group of contaminants has been given great attention due to their behaviour in the environment. They are mostly semi volatile compounds. Examples include industrial

chemicals such as flame retardants chemicals such as PFCs, halogenated compounds used in the production of pesticides like dichlorodiphenyltrichloroethane (DDT) (Janna, 2011).

Pharmaceuticals and personal care products: - this group comprises all pharmaceuticals such as antibiotics, anti-inflammatories such as acetaminophen, antiepileptic drugs and antiseptics, personal care products include chemicals used in soap and detergents, masks and UV protection screens, synthetic hormones like bisphenol A, 17 $\alpha$ ethinyletsradiol and so are also part of this group.

Inorganics: - members of this group include heavy metals such as arsenic, lead and mercury.

Each group of emerging contaminant has some chemicals that can have an impact on the endocrine system. These chemicals are called the endocrine disruptors (Janna, 2011).

#### **2.4.2 Selection of Emerging Contaminants in the Study**

Globally, there is a huge number of emerging contaminants release to the environment. In addition, there is limited available information on their occurrence, fate, and impact on human and wildlife. ECs such as persistent compounds, pharmaceuticals, personal care products and industrial chemicals include a large number of compounds, which are extensively used in the society. For example, there are many types of pharmaceuticals and each group consists of a wide range of compounds with different behaviours.

Hence, it is necessary to choose specific compounds that represent a various groups for investigation. Six types of perfluorinated compounds, bisphenol A and acetaminophen are selected for this study as shown in Table 1.1. The selected compounds in this study are discussed below.

**Table 1.1: Summary Table for groups of emerging contaminants of interest in the study**

Test Type	Chemical Type	Compounds
Chemical	Perfluorinated compounds	Perfluorooctanoic acid Perfluoroheptanoic acid Perfluorononanoic acid Perfluorooctane Sulfonate Perfluorodecanoic acid Perfluoroundecanoic acid
Chemical	Industrial Estrogen	Bisphenol A
Chemical	Acidic Pharmaceutical	Acetaminophen

### 2.4.3 Perfluorinated Compounds

PFCs are a group of organic compounds characterised by a carbon chain. In these compounds, fluorine atoms have substituted hydrogen atoms. PFCs consists of a fully fluorinated hydrophobic alkyl chain R of different length (usually C<sub>6</sub>- C<sub>14</sub>) and a hydrophilic end group X. [R-X] as shown in Figure 2.2 and 2.3. Where R=F(CH<sub>2</sub>)<sub>n</sub>- (Benford et al., 2008).

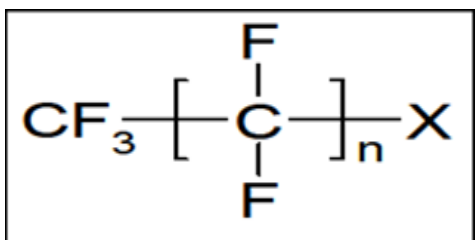


Figure 2.2: General formula of perfluorinated compounds (Benford et al., 2008)

PFCs are a large family of organic compounds. They consist of over a hundred chemicals, which makes the study of their environmental control challenging. They possess unique properties and structures (as shown in Figure 2.3) and can be divided into groups of perfluoroalkyl sulfonates (PFASs) and perfluorinated carboxylic acids (PFCAs). Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are of the greatest concern in this group due to their extensive uses, high concentration level identified in the environment and their toxicity. They are referred to as reference/key compounds for PFASs and PFCAs (Kemikalieinspektionen, 2006; Frommea et al., 2009). However, other groups of perfluorinated compounds such fluorotelomer alcohols (FTOHs), fluorotelomer carboxylates and N-substituted sulfonamides have also gained increased attention. They are used as intermediates in the production of PFAS and as surrogates for PFOS and PFOA (Van Leeuwen & de Boer, 2007; Benford et al., 2008). PFOS and PFOA are made up of a large group of compounds broadly used in industrial applications. They are used as industrial surfactants and surface protectors for paper, food containers, leather, carpets, upholstery, fabric, additives, coating and fire-fighting foams because of their ability to repel water and oil (González-Barreiro et al., 2006). In May 2009, PFCs became emerging contaminants with two of its members, namely perfluorooctane sulfonate (PFOS) and perfluorooctane sulfonyl fluoride (POSF), added to the Annex B list of the Stockholm convention on persistent organic pollutants (POPs).

PFCs are man-made chemicals; they do not occur naturally in the environment but have been produced in large quantities since the 1950s. Concern about perfluorinated compounds (PFCs) is growing because they are globally distributed, environmentally persistent, bioaccumulative, magnify in the food chain and are potentially toxic (Bossi et al., 2008). They occur in the environment chiefly as stable perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS) and perfluorocarboxylic acids (PFCAs) (Bossi et al., 2008).

PFCs are widely used in everyday life and one of the main recipients of these compounds is wastewater treatment plants. When contaminated water is channelled into wastewater treatment plants (WWTPs), the properties and compositions of the contaminants may be altered through the wastewater treatment processes. PFCs are extremely mobile in aqueous systems due to their ionic nature. There are possibilities of these compounds to be transported from wastewater effluents to natural water bodies (Kannan et al., 2006). Release of municipal and industrial wastewaters (WW) has been identified as one of the major

means of introducing organic pollutants such as PFCs into the natural waters (Becker et al., 2008; Pan et al., 2011).

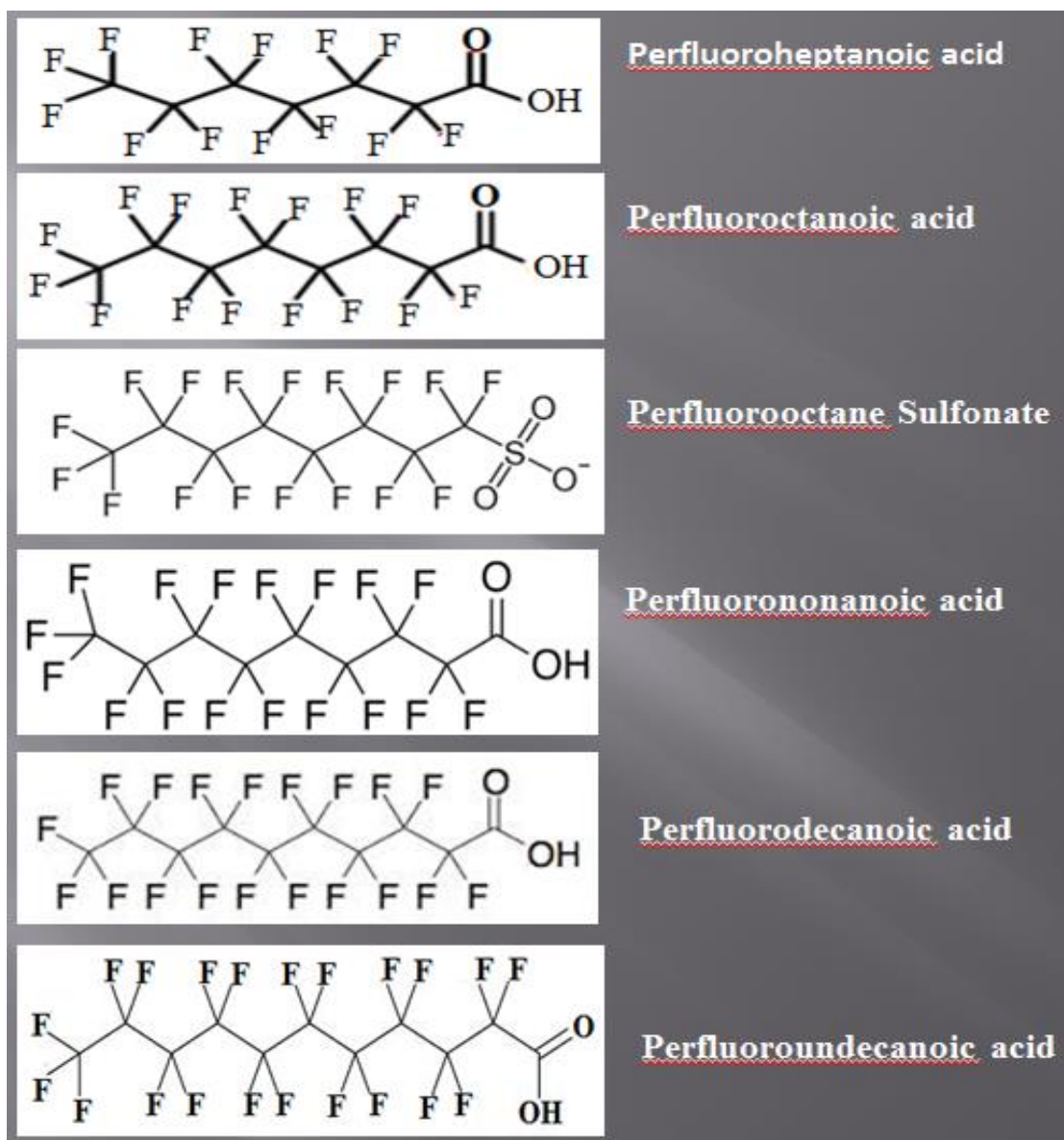


Figure 2.3: Structural formula of selected Perfluorinated compounds.

The persistent and non-degradable properties of PFCs are due to the presence of the extremely strong chemical bonds between carbon and fluorine. (Lange et al., 2006). The hydrophilic end group (X) can be neutral, negatively or positively charged, resulting in non-ionic, anionic, or cationic surface-active agent compounds respectively. Examples of the neutral end groups are the fluorotelomer alcohols (-OH) and the perfluoroalkyl sulfonamides (-SO<sub>3</sub>NH<sub>2</sub>). Examples of the anionic moiety are the sulfonates (-SO<sub>3</sub><sup>-</sup>) e.g. PFOS, the carboxylates (-COO<sup>-</sup>) e.g. PFOA and the phosphate (-OPO<sub>3</sub><sup>-</sup>). The fluorinated hydrophobic part in the cationic PFCs is attached to another end such as the quaternary ammonium group (Kannan et al., 2005; Parsons et al., 2008). The surfactant properties of PFCs are created

when the oleophobic and hydrophobic perfluoroalkyl chains are added to the hydrophilic charged end group such as sulfonates and carboxylates. The hydrophobic nature of PFCs is proportional to their carbon chain length. Different hydrophilic end group shows different behaviour in aqueous environment. Aquatic environment is assumed the main sink for PFCs due to their low vapour pressure and high water solubility (Loganathan et al., 2011). Fluorine possesses the highest electronegativity (3.98) of all atoms, this leads to a strong covalent bond between fluorine and carbon atoms, and this is the most significant characteristic to describe the chemical properties of PFCs (Busch, 2009). The high energy bond between carbon and fluorine, the presence of three (3) pairs of non-bonding electrons in fluorine outermost shell and the small diameter of fluorine atom explains why PFCs are resistant to acids, alkalis, UV light or photolysis, oxidation and reduction (even at high temperatures). Table 2.1 below show the molecular formulas and the molecular weights of the studied PFCs.

**Table 2.1: Information on the six selected PFCs in this study**

<b>Compound Name</b>	<b>Name Abbr</b>	<b>Molecular Formula</b>	<b>Molecular Weight</b>
Perfluoroheptanoic Acid	PFHpA	$\text{CF}_3(\text{CF}_2)_5\text{C OOH}$	364
Perfluorooctane Acid	PFOA	$\text{CF}_3(\text{CF}_2)_6\text{COOH}$	414
Perfluorononanoic Acid	PFNA	$\text{CF}_3(\text{CF}_2)_7\text{COOH}$	464
Perfluorodecanoic Acid	PFDA	$\text{CF}_3(\text{CF}_2)_8\text{COOH}$	514
Perfluoroundecanoic Acid	PFUnDA	$\text{CF}_3(\text{CF}_2)_9\text{COOH}$	564
Perfluorooctane Sulfonate	PFOS	$\text{CF}_3(\text{CF}_2)_7\text{SO}_3$	500

Name abbr. = Name Abbreviated

### 2.3.3.1 Perfluoroalkyl sulphonates (PFASs)

Perfluoroalkyl sulphonates,  $C_nF_{2n+1}SO_3H$  are a group of perfluorinated compounds in which one sulphonate group is attached to the perfluorinated carbon chain. PFAS may be formed when compounds like sulfonamides and polymer (e.g. acrylate polymers) degrade. For example, PFOS is a degradation end product of many perfluorooctanesulfonylfluoride (POSF) based chemicals. POSF based fluorochemicals have been used in many commercial and industrial products for over 4 decades, although the production of these compounds is being regulated (Kannan & Sinclair, 2006). Perfluorooctane sulphonate (PFOS) and perfluorohexan sulphonate (PFHxS) are examples of perfluoroalkyl sulphonates (Kemikalieinspektionen, 2006). PFOS has a sulfonic acid functional group and a straight perfluoroalkyl 8-carbon chain (EPA, 2013).

### 2.3.3.2 Perfluorocarboxylic acids (PFCAs)

PFCAs have the general formula  $C_nF_{2n}COOH$ . They are grouped based on the presence of carboxylic acid chains in the perfluorinated compound. Perfluorooctane acids (PFOA) are an example of PFCAs. PFOA has been given the utmost attention because of its toxic and ecotoxic properties. It is mainly used as a reactive intermediate. PFOA and its salts are used as wetting agents in the production of different fluoropolymers such as polytetrafluoroethylene (PTFE) (Kannan & Sinclair, 2006) and fluoroelastomers. PFOA is applied to produce non-stick coating on cookware (Allsopp et al., 2005). They are employed in some cases in the electronic manufacture and in manufacturing applications as antistatic additives. Other members of PFCA include perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUDA). Naming of these compounds depends on their carbon chain length.

Fluorotelomers is another group of fluorinated compounds. They are industrially manufactured through the process called telomerisation. Unlike the PFAS and PFCA, fluorotelomers are not fully fluorinated, but possess one remaining hydrocarbon group comprising of double (two) carbon atoms ( $-CH_2CH_2-$ ). Fluorotelomers are perhaps the most frequently used perfluorinated compounds in products. The film forming features and tendency of fluorotelomer to reduce fuel absorption make it useful in the manufacturing of firefighting foams (Christensen & Li, 2014). In 2006, the global production of fluorotelomers was valued at 20 million pounds. The United States of America accounts for

over 50% of the global production of fluorotelomers. Textiles and clothing companies accounts for almost 50% of the total volume (EPA, 2009).

The presence of hydroxyl groups as functional group in fluorotelomer will produce fluorotelomer alcohols (FTOH). Fluorotelomer alcohols are often mass-produced as raw material in the production of polymeric products and fluorotelomer-based compounds. They have been highlighted to be the main starting compounds of numerous perfluorocarboxylic acids (PFCAs) and are manufactured as a mixture containing primarily six to twelve fluorinated carbon chains. Fluorotelomer alcohols (e.g.  $n = 6, 8, 10, 12$ ) exists in these products as residual raw materials (De Voogt et al., 2006; Kemikalieinspektionen, 2006).

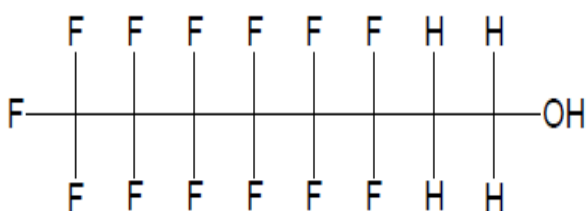


Figure 2.4: Structural formula of fluorotelomer alcohol.

### 2.3.3.3 Physicochemical properties of PFCs

Many PFCs are similar to persistent organic pollutants (POPs) in terms of their stability and hydrophobicity. In this case, perfluoroalkyl sulfonates (PFASs) are different, possessing both oleophobic properties in one end of the molecule and sometimes hydrophilic or polar properties in the other functional end, while POPs are mainly non-polar and lipophilic. Generally, PFASs are very stable substances. They have low vapour pressures, special surface-active properties and surface energies. PFOS are slightly water soluble, thermal stable, non-volatile, and a strong acid. Thus, they can completely dissociate to ionic form in water at pH 7.

The PFOS anion is able to form strong ion pairs with several cations. Log  $K_{ow}$  values of PFOS cannot be measured because of their surface-active properties and the very low  $PK_a$  value (-3.27) also shows that PFOS is considered as a strong acid and this compound will be present in the environment totally in the ionized form. They have been listed as type II, compounds with very low volatility (OECD, 2002). Estimated water solubility of PFOA is 3.4 g/L, indicating that PFOA is highly soluble in water compared to PFOS. It is present as an anion in solution. It has a boiling point of 189°C. The physicochemical properties of PFCs are shown in Table 2.2, (Loganathan et al., 2011).

**Table 2.2: Physicochemical Properties of selected PFCs** (Suja et al., 2009; Vecitis et al., 2009; Loganathan et al., 2011)

n.a. = not available

Compound	Solubility in pure water( g/L)	Vapour Pressure	Log K <sub>ow</sub>	Melting Point (°C)	Boling Point (°C)	PK <sub>a</sub>	Density (g/cm <sup>3</sup> )
Perfluoroheptanoic Acid (PFHpA)	n.a.	n.a.	n.a.	24-30°C	175	n.a.	n.a.
Perfluorooctanoic Acid (PFOA)	3.4	10mmHg	3.60	45-50	189	2.8	1.8
Perfluorononanoic Acid (PFNA)	n.a.	n.a.	4.50	71-77	218	2.5	n.a.
Perfluorodecanoic Acid (PFDA)	n.a.	n.a.	5.40	n.a.	219	n.a.	n.a.
Perfluoroundecanoic Acid (PFUnDA)	n.a.	n.a.	n.a.	n.a.	160	n.a.	n.a.
Perfluorooctane Sulfonate (PFOS)	0.57	3.31x10 <sup>-4</sup> Pa@ 20 <sup>0</sup> C	4.30	≥400	133	-3.27	n.a.

## 2.4.4 Degradation and Transformation of Perfluorinated Compounds

PFCAs and PFASs have been classified as the most persistent groups of perfluorinated compounds. They are non-biodegradable and resistant to basic and acidic attack, hydrolysis, photolysis, oxidation and reduction. Reports on the hydrolysis and aqueous photolytic decomposition of PFOA indicated that this compound has a longer life in the environment. Most PFCs do not respond to oxidation by potassium permanganate ( $\text{MnO}_4^-$ ) or potassium dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) (Qiu, 2007). Some methods of degrading by sonochemical decomposition of PFACs with oxidative techniques such as UV, UV/ $\text{H}_2\text{O}_2$ , UV/persulfate and heteropolyacid photocatalysts under severe conditions have been reported to be suitable for wastewater treatment (Lange et al., 2006).

Hori et al. (2004) carried out decomposition of PFOA and PFCAs in water by photochemical methods (UV, UV/ $\text{H}_2\text{O}_2$ , heteropolyacid photocatalyst). UV/ $\text{H}_2\text{O}_2$  was found to be less productive in PFOA degradation when compared to the direct UV, which produced  $\text{CO}_2^-$ , fluorine ion and shorter chain perfluorocarboxylic acids. Heteropolyacid photocatalysts could effectively decompose PFOA with the production of  $\text{CO}_2^-$  and fluorine ion.

Meesters and Schröder. (2004), examined degradation of PFOS and PFOs under aerobic and anaerobic conditions in the laboratory with closed-loop set up. Under anaerobic conditions, successful removal of PFOA and PFOS from wastewater samples was observed, while degradation under aerobic conditions was not effective.

### 2.3.4.1 PFCS bioaccumulation

For over 50 years, PFCs have been produced and used in many products globally. These compounds can be discharged into water bodies through a point source (municipal and industrial treatment plants) and non- point sources (atmospheric and surface runoff) release. They can be assimilated by aquatic organisms and find their way into the ecosystem via distribution and bioaccumulation in the food chain, therefore possibly become a health hazard to humans and animals (Suja et al., 2009). The characteristics of the selected PFCs as represented in Table 2.2 show that these compounds possess low vapour pressure and are soluble in water. Consequently, most PFCs released into aquatic environment would possibly remain in the aqueous medium, except adsorbed onto particulate matter (Fujii et al., 2007). Global analysis of the bioaccumulation and the biomagnification potential of PFCs in environmental samples have indicated PFCAs (with C8 - C15 chain lengths), PFHxS, PFOS

and FOSA as globally persistent organic pollutants. Studies have shown that PFCs such as PFOS and PFOA are polar surfactants and ions, thus accumulate in tissues, liver and kidney and bind to the blood proteins. Unlike other persistent organic pollutants, such as the polychlorinated biphenyls (PCBs) and polybrominated biphenyl ether (PBDEs), these compounds do not amass in fatty tissues (Kannan et al., 2001; Lange et al., 2006).

In Japan, Taniyasu et al., (2003) investigated levels of PFCs bioaccumulation in wild fish from various regions. PFOS compounds were identified in all the fish tissue samples. The estimated bioaccumulation factor for PFOS for one species of freshwater, marine fish and two marine species ranged from 274 – 41600.

#### **2.3.4.2 Sources of perfluorinated compounds in the environment**

Knowledge of PFCs source and fate in the environment is important and necessary in order to understand their behaviour in the environment. From 1951 to 2004, global production of PFOA and its ammonium salt was estimated to be 3600 – 5700 tonnes. Production of total PFCAs was also estimated to be 4400-8000 tonnes and the total discharge to the environment was 3200-7300 tonnes (Prevedouros et al., 2006). In the last 10 years, PFASs emission to the environment was estimated to be 4650 tonnes per annum. Due to its toxicity, there has been legislation in its production and uses in some countries. Although the use of PFOA is limited in developed countries, they are still detected in some consumer products, mostly water, grease, and stain repellent products. This indicates extensive and dispersive sources of PFOA into the environment. Additionally, sources of PFCs include discharge at production, during their use in the production of consumer products, also from WWTPs and landfills after their use. The aquatic environments in developing and industrialized regions such as Europe, America, Japan and China have been found to be extremely contaminated with PFCs. Direct effluent discharge from firefighting foam production, fluorochemical, perfluoroelastomers and perfluoropolymers manufacturing has also been suspected as source of PFCs in the environment (Armitage et al., 2006; Vierke et al., 2012). High PFC concentration levels have been detected in regions near industrial point sources such as Dupont in New Jersey, West Virginia of USA and 3M in Minnesota (Oliaei et al., 2013).

Globally, several studies on PFCs show their extensive occurrence in the environment and other media. PFOS and PFOA are the two most studied PFCs. They have been detected in wastewater treatment plants (WWTPs) and river water (Becker et al., 2008; Bossi et al., 2008; Murakami et al., 2008; Sun et al., 2011; Pan.YuanYuan et al., 2011; Arvanitia et al., 2012; Kim et al., 2012), in surface and drinking water (Skutlarek et al., 2006; Senthilkumar

et al., 2007; Ericson et al., 2008; Mak et al., 2009; Wilhelma et al., 2010), in sediments and soil (Kannan et al., 2005; Senthilkumar et al., 2007; Bao et al., 2009; Naile et al., 2010; Yang et al., 2011; Becker et al., 2008), in fish (Senthilkumar et al., 2007; van Leeuwen et al., 2009), and in maternal cord and house dust (Beesoon et al., 2011). In humans, 0.135 - 2.44 mg/L of PFOS and 0.106 - 6.8 mg/L of PFOA have been detected in the serum of fluorochemical manufacturing workers. Also concentration ranges of 0.017 – 0.053 mg/L and 0.003 – 0.0117 mg/L of PFOS and PFOA respectively, were detected in the general public (Hekster & De Voogt 2002). 17 – 53 µg/L and 3 - 17 µg/L of PFOS and PFOA.

Sinclair et al. (2006) in a study on the occurrence of perfluoroalkyl surfactant in wastewater effluent from New York State, found PFOA concentration (58 – 1050 ng/L) to be higher than those of PFOS (3.0 – 68 ng/L). Remarkably high PFOS concentrations of 198 – 1,090 ng/L were reported in Lake Onondaga. This was attributed to the use of fluorotelomer and telomer alcohol in the area and the volume of industrial effluent discharged into the lake. Therefore, industrial discharges were speculated to be a major source of PFOA and PFOS pollution in the New York surface water (Sinclair & Kannan, 2006).

In a study of the water quality of Yodo River basin, Japan, Lien and coworkers. (2006) analysed the level of PFOA and PFOS in treated effluent released from some sewage treatment plant into Osaka bay via Yodo River, Japan. PFOA and PFOS concentrations of the effluents ranged from 25 – 922 ng/L and 3 – 76 ng/L, respectively. Their mass loadings were negligible. It ranged from 0.03 – 45 g/d and 0.005 – 15 g/d, for PFOA and PFOS respectively. While municipal wastewaters and atmospheric transport can contribute to the pollution problem, the data obtained in the study shows no proper correlation between population numbers and compound mass loading. Hence, industrial discharges into the sewage treatment plants were hypothesized to be a source of PFOA and PFOS pollution.

In Japan, potable water from nine different waterworks was analysed for the presence of PFOS. Low concentrations, which ranged between 0.1 - 4.0 ng/L were observed in eight waterworks. High PFOS concentrations of 43.7 ng/L and 50.9 ng/L were detected in only one waterworks. The high concentration was explained by the fact that the waterworks water source is from Tama River, which is polluted with PFOS by a wastewater treatment plant in the area (Harada et al., 2003).

Doug. (2010) also made the following conclusions from the results obtained in the analysis of PFCs in Washington wastewater treatment plant effluents, rivers, lakes, and on fish meat.

(i) The Concentration of PFCs in wastewater treatment effluent was steadily higher compared to lakes and rivers. (ii) Low concentration of PFCs were detected in rivers without wastewater treatment discharge and (iii) the concentration of PFCs does not change with season, except for perfluoroheptanoic acid (PFHpA) which was detected more in spring than in the summer. Furthermore, high levels of PFCs were observed in human, wildlife, and the environment close to industrial/urbanised regions compared with rural or remote regions (Allsopp et al., 2005). These facts point to the manufacturing process as a source of PFC contamination in the environment.

Although wastewater treatment and recycling methods have been developed to minimize PFCs releases rate, the existing water and wastewater treatment methods have proved to be ineffective for total level of PFCs removal. This is due to the degradation of volatile PFC precursors, which have been identified as another source of PFCs in the treatment effluent and the environment. Loganathan et al. (2007) studied the contamination level of some PFASs and PFACs at various phases of wastewater treatment in Kentucky and Georgia (USA) WWTPs. Concentration of PFOS and PFOA in Kentucky WWTP ranged from 7.0 – 149 ng/L and 22 – 334 ng/L, respectively. The PFOS and PFOA concentration in Georgia WWTP ranged from 1.8- 22 and 1-22 ng/L, respectively. Concentrations of PFCs, mostly PFOS and PFOA, in the effluents were found to be greater than the concentrations of the influents. The increase in the effluent concentration after various phases of treatment indicates additional sources of PFOS and PFOA within the treatment stream, which was later suggested to be from the breakdown of fluorinated precursors during the treatment process.

In South Africa, PFCs have been reported in raw and drinking water in the Western Cape (Booi, 2013), in the maternal serum at a concentration of 1.6 ng/mL, 1.3 ng/mL, and 0.5ng/mL for PFOS, PFOA and PFHxS respectively, and also in the placental cord blood at a concentration of PFOA (1.3 ng/mL), PFOS (0.7 ng/mL) and PFHxS (0.3 ng/mL) (Hanssen et al., 2010). Furthermore, there is limited data available on the PFCs contamination in wastewater effluent, which has been listed as one of the likely sources of pollution to the environment (Kannan & Sinclair, 2006) and the efficiency of its removal through wastewater treatment plants have not been reported in South Africa. PFCs have been recognized to be toxic, resistant to ecological degradation and therefore become pervasive in the environment through the solid and wastewater processes given their resilience to degradation during wastewater treatment (Oscar & Shanea, 2009).

#### **2.3.4.3 Levels in ground and drinking water**

In the introduction of this study, it has been established that PFCs are globally present in the environment. Results from a study by Steenland et al. (2009) shows that adults: (1) who often drink well, rather than bottled water (2) who work or reside nearby PFC plant (3) who consume locally produced vegetables, had higher levels of PFOA in their blood.

In Japan, the level of PFOS ranged between 0.1 – 4 ng/L in tap water from eight different waterworks. In addition, a higher concentration (50ng/L) was identified in tap water from another waterworks, which receives water from contaminated rivers (Harada et al., 2003).

In a study by Boiteux et al. (2012), 10 PFCs were analysed in both raw and treated drinking water. Perfluorohexanoic acid (PFH<sub>x</sub>A) had the highest concentration of 139 ng/L in the raw water while PFH<sub>x</sub>A had the highest concentration (125 ng/L) in the treated water. PFH<sub>x</sub>S, PFH<sub>x</sub>A, PFOS and PFOA were the predominant compounds among the studied PFCs. The levels of PFOA and PFOS observed in the treated water were lower than the health related values for drinking water, as specified by different countries (Boiteux et al., 2012).

#### **2.3.4.4 Route of human exposure**

The extensive use and huge historical manufacturing volumes of PFCs in consumer products suggest a potential for PFCs contamination in food, drinking water and in both indoor and outdoor environments (through dust inhalation). Some researchers have monitored these substances in human blood and serum samples and have convincingly indicated the ingestion of contaminated water, food and regular usages of PFCs-containing materials as the major source of PFCs to human. Ericsson et al. (2008b) examined the dietary intake of PFCs by determining their presence in several foodstuffs, and the consumption of such foodstuffs. The result obtained from the study does not justify dietary intake as the main route of exposure. This clarifies that there are other routes such as water contributing to the presence of PFCs in humans. Furthermore, a correlation between dietary intake and blood level of PFOS was suggested.

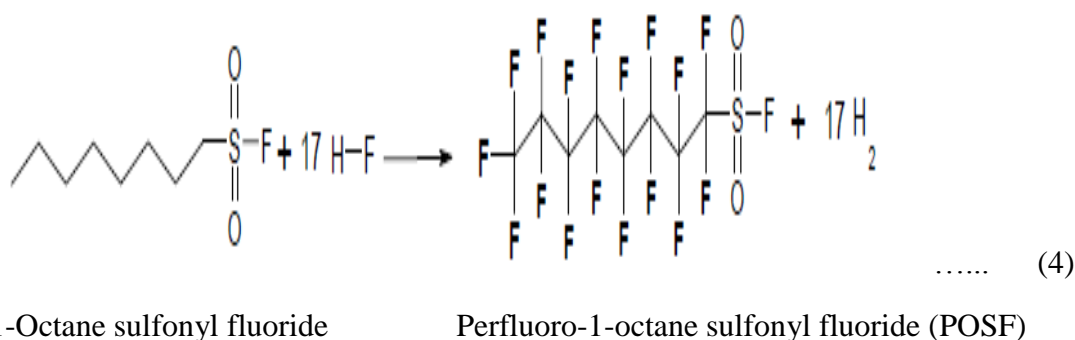
In several cases, contaminated water has been discussed to be the main source of PFCs exposure (Ericson et al., 2008; Wihelm et al., 2010; Domingo et al., 2012; Post et al., 2013). Hölzer and co-worker. (2008) found that the consumption of polluted tap water was proportional to the occurrence of PFOA concentration in human blood serum. Also,

consumption of contaminated locally produced vegetables and fruit as well as fish from local rivers and lakes are related to PFC concentration in the blood plasma of the local population. This justifies the argument that drinking water is a possible route of PFCs into the human system.

#### 2.4.5 Production of Perfluorinated Compounds

In 2002, the 3M Company, the major producer of PFCs discontinued the production of perfluorooctanesulfonylfluoride (POSF) - based products and this was replaced with butyl-based materials. Nevertheless, there remain several manufacturing industries such as textile, semiconductor and paint industries that still use PFCs in their manufacturing processes and produce PFOA and PFOS-based consumer products (Suja et al., 2009). Perfluorinated compounds are synthesized through two major processes: electrochemical fluorination (ECF) and telomerisation (TM). In the production of PFCs, the final product may further react to give various derivatives and polymers (Kemikalieinspektionen, 2006).

In the electrochemical fluorination (ECF) process, perfluorinated compounds are produced by direct fluorination. The organic compounds to be fluorinated are dissolved or dispersed in anhydrous hydrogen fluoride and a direct electric current (5-7eV) is passed through anhydrous hydrogen fluoride. All the hydrogen atoms in the organic compound are then replaced by fluorine atoms (Hekster & De Voogt 2002; Parsons et al., 2008). Products with even and odd numbers of carbon chain length can be generated. This process yields mixtures of perfluorinated compounds. For example, C<sub>8</sub> starting material yields products ranging from C<sub>4</sub> to C<sub>9</sub>. Branched chain products can also be formed. Thus, the products of this process contain many impurities (Hekster & De Voogt, 2002; Kemikalieinspektionen, 2006)

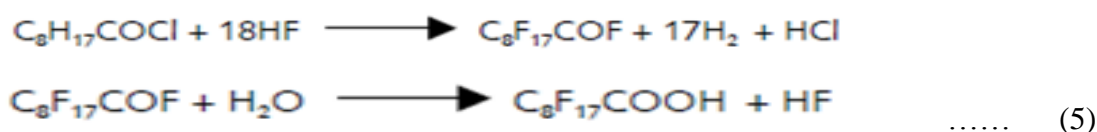


(Example of electrochemical fluorination (ECF) process)

Perfluorooctane sulfonate (PFOS) is produced by ECF process. The starting chemical is 1-octanesulfonyl fluoride, which gives an initial product of perfluorooctanesulfonyl fluoride

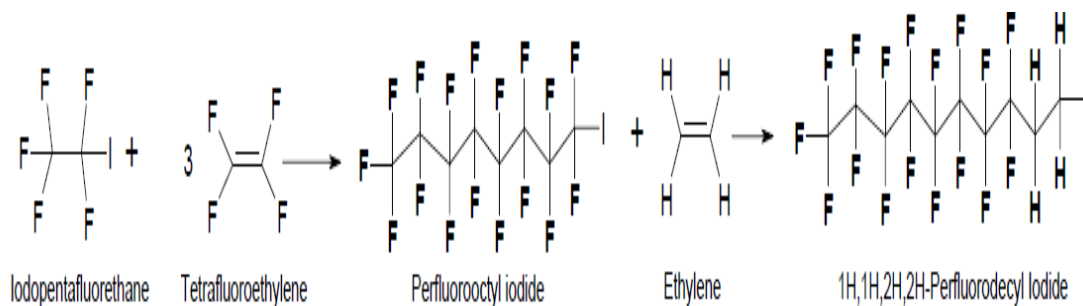
(POSF) as shown in the Equation 4 above. POSF is used as an intermediate in the production of other chemicals such as PFOS, which is produced by the hydrolysis of POSF. The 3M Company have used ECF process from 1950s through 2001 to synthesise PFOS, perfluorooctane sulfonamide ethanols (FOSEs) and perfluorosulfonamide (PFOSA). PFOSA and FOSEs have been discovered to degrade to PFOA (through biotic degradation) and PFOS (through both biotic and abiotic degradation).

PFOA can also be produced from octanoyl chloride using the ECF process. Hydrolysis of the obtained product (perfluorooctanoyl fluoride) yields PFOA.



Production of PFOA with ECF process (Hekster & De Voogt, 2002)

Since the 1970s, the telomerisation process has been employed in the production of fluorotelomer olefins, fluorotelomer acrylates, fluorotelomer alcohol, fluorotelomer iodide and perfluoroalkyl carboxylates. Perfluorinated alkyl chains are produced from the reaction between iodopentafluoroethane and tetrafluoroethylene. This process produces straight chains with even numbers of carbon chain lengths (generally C6, C8, C10 and sometimes C12).



Example of telomerisation process ..... (6)

### 2.4.6 Toxicity of Perfluorinated Compounds

Liver has been identified as the major target organ for PFCs. Perfluorocarboxylates have been identified to cause peroxisome proliferation in rat liver, affect mitochondrial, microsomal, cytosolic enzymes and proteins involved in lipid metabolism (Kawashima et al., 1995; Cheng & Klaassen, 2008). Generally, PFOS appears to be more active than PFOA regarding this effect, PFDA (PFC with a longer alkyl chain) have been found to be more

active. PFOA and PFOS were found to cause extensive toxic effects like liver cancer and testicular cancer, respectively on laboratory rats exposed to these compounds. USEPA have listed PFOA as carcinogenic in wildlife.

PFOA and PFOS were found to reduce serum cholesterol and involve in the induction of enzyme related to  $\beta$ -oxidation of fatty acids. PFOS caused negative effects on growth and caused death of rat pups. PFOS was found to affect the estrous cycle in rats. Therefore, it can be referred as an endocrine disruptor. PFOA also affects the immune system and reduce body weight (Poulsen et al., 2005).

#### **2.4.7 Perfluorinated Compounds Legislation**

In 2008, the European Food Safety Authority (EFSA) and the German Federal Institute published an assessment of the potential risks of PFOA and PFOS in foodstuffs on human health for Risk Assessment. PFOS and PFOA were the only two PFCs considered in the study on the risk evaluation. Their negative effects on the general population were questionably centred on the identified PFCs concentration in foodstuffs and serum samples and the current level of scientific knowledge. Nonetheless, uncertainty in the risk evaluation was observed and the data available were inadequate for the foodstuff diversity (Stahl et al., 2011). In 2009, the United States Environmental Protection Agency (USEPA) issued a provisional health advisory for the maximum limit of 400 ng/L PFOS and 200 ng/L PFOA in drinking water (USEPA, 2009). There is a partial existing national controlling regulation USA that defines a specific concentration level for all PFCs. Some states have declared a health risk limit for some PFCs in drinking water. Minnesota 0.3  $\mu\text{g/L}$  for PFOS and PFOA, 0.04  $\mu\text{g/L}$  in New Jersey and 2  $\mu\text{g/L}$  for PFOA in North Carolina (EPA 2012; Oliaei et al., 2013). Besides, USEPA identified PFCs for an action plan development based on their presence in human blood, their persistence, bioaccumulation and toxic nature as part of the struggle to improve the current chemicals program under the Toxic Substance control Act (TSCA). There have been regulations on textile products in some countries. A maximum limit recommended for PFOS in textile products in the European Union (EU) is in  $\mu\text{g/m}^2$ . No limits are in place for the other PFCs in countries with strong regulation of PFOS in textile products, even with concerns about their harmful nature. In addition, they can regularly be present at a very high concentration in the textiles. In Norway, a legislation that banned PFOA in consumer products and the sales of textile products containing  $\geq 1\mu\text{g/m}^2$  PFOA was introduced in June 2014 (Brigden et al., 2014). Since it has been discovered that perfluorooctane sulphonate (PFOS) has serious negative impact on human, wildlife and the

environment, all PFOS related compounds are being phased out and many manufacturers have focused on other fluorinated compounds with the same required properties in order to replace PFOS. Unfortunately, several replacement compounds have also shown to relate to negative impacts on human, wildlife and the environment (Kemikalieinspektionen, 2006).

## **2.5 ACETAMINOPHEN**

Pharmaceuticals are a group of potential endocrine disrupters (EDs). These compounds and their metabolites are subclasses of organic environmental contaminants and have lately attracted great attention of the global scientific community. They are widely and increasingly being used in human and veterinary medicine. Pharmaceuticals are produced to have a precise mode of action while many are persistent in the body (Khamis et al., 2011).

Acetaminophen (Paracetamol), also known as 4-acetaminophenol with IUPAC name 4'-Hydroxyacetanilide, or 4 -acetamidephenol or Tylenol is a readily available over-the-counter pain reliever (analgesic) and fever reducer (antipyretic). It is used to treat conditions such as headache, muscle aches, arthritis, backache, toothaches and minor pains such as flu and period pain. As an analgesic, acetaminophen's main property is the prevention of cyclooxygenase and the inhibition of conversion of arachidonic acid to prostaglandin metabolites. Acetaminophen is also used in veterinary medicine. In pigs and poultry it has been used for treatment associated with fever. In livestock, it is used in the treatment of fermentation disorders and high level of acetone in the blood (acetonemia). Other uses of acetaminophen include as intermediate for other pharmaceuticals, fabrication of photographic chemicals and azo dyes and as hydrogen peroxide additive (Carla, 2013).

### **2.5.1 Production and Use of acetaminophen**

Human pharmaceuticals are often released into the environment after their ingestion and following excretion through the wastewater treatment network. Additionally, the inappropriate disposal or flushing of unused medicines through toilet systems, improper disposal of hospital wastes, poor treatment of manufacturing waste and intensive animal farming can also contribute to the overall problem. Globally, these compounds have been detected at low concentrations (ng/L to µg/L) in different environmental samples such as wastewater treatment plant effluents (Gómez et al., 2007), drinking water (Petrovic et al., 2013; Castiglioni et al., 2014), surface, and groundwater (Thomas et al., 2007; Fram & Belitz, 2011; Hedgespeth et al., 2012). Despite their presence at low concentration, their negative effects on sensitive aquatic organisms cannot be excluded (Huber et al., 2005).

Different potential negative effects such as accumulation in tissues, acute and chronic damage, behavioural change, inhibition of cell proliferation and reproductive damages have been recorded at these very low levels (Escher et al., 2011). Nonsteroidal anti-inflammatory drugs (NSAID) such as acetaminophen, aspirin (acetylsalicylic acid) and ibuprofen are examples of the most predominant pharmaceuticals in treated wastewater. They are frequently used due to their ready availability over the counter and access to purchase without prescription.

There has been an increased concern about the possible effects of acetaminophen on the environment and human health due to its frequent identification in drinking water and aquatic environments. Globally, there has been an increase in the consumption of acetaminophen. In 2000, acetaminophen was listed as one of the top three drugs prescribed in England, and one of the top 200 prescribed drugs in USA. Between 1978 and 1988, acetaminophen use increased fivefold in Nordic countries and between 1994 and 1995, the rates in some developed countries exceeded 20g per person per year. In UK, the consumption of prescribed and un-prescribed acetaminophen and other tablets containing acetaminophen is 3.5 billion of 500 mg tablets in 2000 (Ranieri et al., 2011). Acetaminophen consists of a benzene ring core, which is substituted by one hydroxyl group and nitrogen atom of an amide group in the para (1, 4) pattern (Wu et al., 2012)

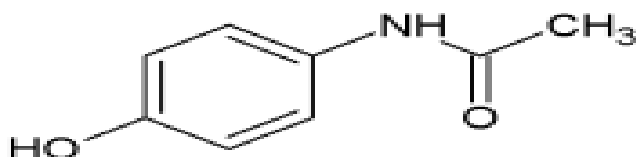


Figure 2.5: Chemical structure of Acetaminophen

### 2.5.2 Properties and Occurrence

Presently, there is no known record on the natural occurrence of acetaminophen. Solubility of acetaminophen in water is far lower than in other polar solvents like ethanol. They have high melting point of 170°C, relative molecular mass 151.17 and density of 1.293 g/cm<sup>3</sup> at the temperature of 21°C. Table 2.3 below presents the physical and chemical properties of acetaminophen compounds.

**Table 2.3: Physical and chemical properties of pure acetaminophen compound (IARC, 1999)**

<b>Description</b>	<b>White crystalline powder</b>
<b>Melting point</b>	170°C
<b>Molecular formula</b>	C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub>
<b>Relative molecular mass</b>	151.17
<b>Density</b>	1.293 g/cm <sup>3</sup> at 21°C
<b>Solubility</b>	Low solubility in water; very soluble in ethanol
<b>Octanol/water partition coefficient</b>	log P, 0.31
<b>Conversion factor</b>	mg/m <sup>3</sup> = 6.18 × ppm

### 2.5.3 Acetaminophen in the Environment

Acetaminophen has been quantified in conventional secondary WWTPs effluent at some µg/L levels (Nödler et al., 2010). The compound is subject to different biological and chemical transformation processes, including hydrolysis, biodegradation, photolysis and bioaccumulation (Trovo et al., 2008). The properties including toxicity and persistence of acetaminophen degradation products have not been extensively discussed in the literature. It is slightly soluble in water but easily accumulate in the aquatic environment. It has been identified to occur at high µg/L levels in hospital effluents and WWTPS inflow. This compound has also been found to be effectively removed by some wastewater treatment process (Thomas & Langford, 2007). Furthermore effective removal by WWTPs results in low ng/L levels being detected in WWTP effluents. In a study by Kim et al. (2012), concentration of up to 76 µg/L acetaminophen was detected in wastewater treatment

influent and 0.224 µg/L in the effluent. There have been concerns over the behaviour of acetaminophen during wastewater and potable water treatment. Chlorination is one of the most common water treatment processes. Unlike PFOA, PFOS and some other pharmaceuticals, acetaminophen is easily degraded and removed by the sewage treatment plants. Sewage effluents and rivers in Germany was investigated, acetaminophen was not detected in river water and was only detected in less than 10% of all sewage effluents. In the US, 142 streams susceptible for contamination by municipal sewage effluents were investigated. Acetaminophen was detected in 17% of all samples at maximum levels up to 10 µg/L (Kolpin et al., 2002). A study by Muir et al. (1997) also shows that 58 to 68 % of acetaminophen and their metabolites are expelled from the body during therapeutic use.

#### **2.5.4 Acetaminophen Health Effects**

Although acetaminophen has been reported not extremely persistent in the environment, it has also been shown that its continuous environmental release overrules its high transformation rate; hence, it can have negative effects on aquatic organisms. Acetaminophen has been reported to cause severe toxicity effects in the aquatic invertebrate *Daphnia magna*, in bacterium *Vibrio fischeri* and in fish *Oryzias latipes* (Santos et al., 2013).

### **2.6 BISPHENOL A**

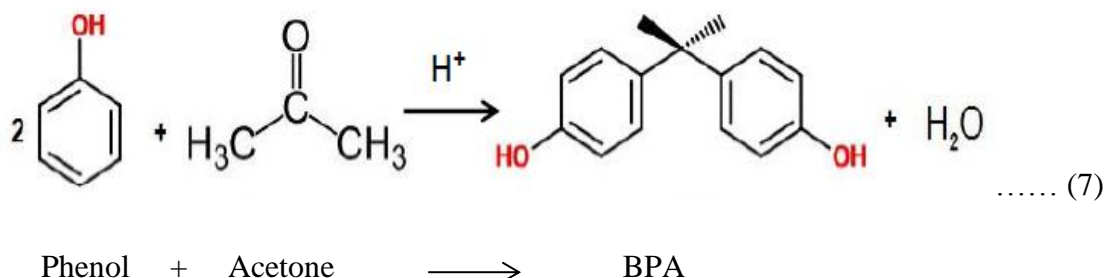
The occurrence of endocrine disrupting compounds (EDCs) in the water cycle (from wastewaters to aquatic systems to drinking water) has been of major environmental concern. EDCs can be referred to as various exogenous substances that have negative effects on human and aquatic life, or their progeny, thereby resulting in alterations to endocrine function. The chemicals affect reproduction, growth and development. They include various groups of heterogeneous chemicals such as alkyl phenols, polychlorinated biphenyls, steroid sex hormones, certain pesticides, and phthalates (Pothitou & Voutsas, 2008). They have been identified in domestic and industrial wastewater effluents, landfill effluents and livestock wastes (Ying et al., 2002; Olujimi et al., 2013). Among these compounds, Bisphenol A has attracted attention due to its extensive applications.

#### **2.6.1 Production of Bisphenol A**

BPA was first synthesized in 1891. It is synthesized from the combination of two moles of phenol with one mole of acetone in the presence of sulphonated styrene divinylbenzene catalyst or HCl. The reaction is often catalysed at a temperature of 60-80°C. It is

synthesised by two different techniques. The first technique involves the condensation of phenol with acetone under high temperature, low pH and in the presence of catalysts. The raw compound obtained is then purified by distillation. Liquid purified compound is further filtered and dried.

The second method is similar to the first but different catalysts and purification methods are used. This method produces fewer wastes. The dried BPA synthesised by both techniques is in flakes, prill or crystal form. BPA may be accidentally released into the environment as dust emission from closed systems during manufacturing or by poor handling, packaging and transportation (Staple et al., 1998). Equation 7 below shows the chemical reaction for the formation of BPA.



Chemical reaction for the formation of BPA (Farooq, 2015)

### 2.6.2 Bisphenol A Uses

BPA as a synthetic chemical is used as an intermediate in the plastic industry for the production of epoxy resins, flame-retardants, polycarbonate plastics and some other domestic products. It is also used in the manufacture of thermal paper to some extent. Plastics produced from BPA are used in food and drink packaging to line bottle tops, metal food cans, and water supply pipes.

Most human exposures to BPA are from their use in beverage and food containers. They can leach into food from polycarbonate plastic products and from containers lined with epoxy resin coatings. Some polymers used in dental treatment also contain this compound (Fürhacker et al., 2002). Several wastes containing BPA are released into the environment during manufacturing, poor handling, leaching, heating, and uploading and through accidental spills (Staple et al., 1998). Because of its extensive usage both in industry and households, its presence can be expected in raw sewage, wastewater effluents and concentrated in sewage sludge (Olujimi et al., 2013).

### 2.6.3 Properties of Bisphenol A

Under normal conditions, BPA appear as prill, flakes or crystal solids. BPA has a high melting point, low vapour pressure and is slightly soluble in water (120 – 300 mg/L at pH 7). Due to its dissociation constant (PKa 9.6 – 10.2), BPA has higher solubility at basic pH values. Based on the reported log K<sub>ow</sub> values, BPA is considered to have moderate or low hydrophobicity and therefore, a low capacity to bioaccumulate.

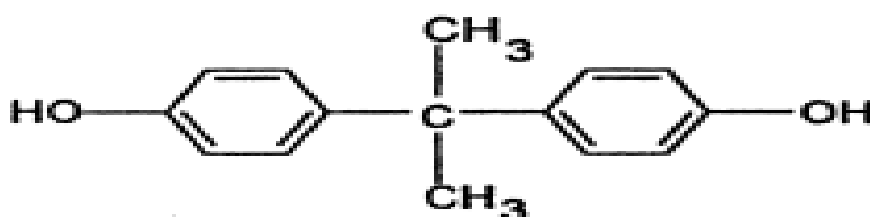


Figure 2.6: Chemical structure of Bisphenol A (Fürhacker, Scharf and Weber 2000)

Table 2.4: Physicochemical properties of Bisphenol A

PROPERTIES	VALUE
Molecular weight	228 g/mole
Empirical formula	(CH <sub>3</sub> ) <sub>2</sub> C(C <sub>6</sub> H <sub>4</sub> OH) <sub>2</sub>
Specific gravity	1.09 - 1.19 g/cm <sup>3</sup>
Boiling point	398 °C
Melting Point	150 - 155 °C
Log Kow	3.4 (3.3 - 3.8)
Solubility	120 - 300 µg/mL @ pH7
Vapour pressure	8 E <sup>-10</sup> – 4 E <sup>-7</sup> mm Hg
Henry's constant	10 <sup>-10</sup> Atm-m <sup>3</sup> /mol
pKa	9.6 - 11.3

<b>Log Kow</b>	2.30 - 3.82
<b>Density</b>	1.20

#### 2.6.4 Presence of BPA in the Environment

BPA is a pseudo-persistent substance. Despite its short half-life, it is abundant in the environment due to its continuous release. Wastewater treatment plant effluents and landfill leachates have been identified as the primary source of BPA environmental contamination (Fürhacker et al., 2000; Kang & Kondo, 2006). BPA solubility in water ranges from 120 – 300 mg/L (Table 2.4). Because BPA cannot be totally removed during the wastewater treatment process, wastewater containing this chemical can be a source of contamination to the environment. BPA has been detected in wastewater effluents from plastic manufacturing companies and waste paper recycling plants (Olujimi et al., 2013). In addition, its release from BPA based products and the natural breakdown of polycarbonate plastic is one of the routes of BPA contamination in the aquatic environment. In USA, 1266 metric tons of BPA were recorded as released through off-site transfers for incineration and to municipal wastewater treatment plants. Manufacturing processes also release over 577 metric tons in one year (in 2008). Additionally, the use and flushing of toilet paper into toilets has been identified to contribute to high level of BPA in municipal wastewater. BPA and alkyl phenol polyethoxylate surfactants are used in paper production; therefore, contamination of recycled paper products with these compounds can be expected. Contamination of wastepaper, toilet paper and cellulose samples with BPA has been investigated by Gehring and co-workers (2004). BPA concentrations of up to 46mg/kg dm were identified in tissue papers (Gehring et al., 2004). The levels of BPA detected in different environmental media, as well as its global documented presence, show that:

- (i) BPA was present in detectable concentrations in wastewater and wastewater sludge and extensively distributed in the environment,
- (ii) BPA is stable in matrices including wastewater and wastewater sludge and does not break-down rapidly, and
- (iii) Taking mass balance into consideration, it was found that the rate of entry of the contaminant and the amount entering into the environment is greater than the rate of degradation which results in high detection levels (Mohapatra et al., 2011)

In the United States, the concentration of BPA found in drinking water treatment plants is about 420 ng/L and higher concentrations of up to 3,642 ng/L in municipal WWTPs

(Stackelberg et al., 2004; Huang et al., 2012). Additionally, in 2002, the United State Environmental Protection Agency (USEPA) assessed the amount of BPA released into the environment yearly. 85,300 kg was estimated emitted to the air, 3,500 kg released directly to water bodies, 1,100 kg to receiving water after up to 90% removal in wastewater treatment plants, and 10,000 kg into water through indirect sources such as landfills (Farooq, 2015). High levels of BPA were found in landfill leachates at concentration ranges of 1.29 – 17,200 µg/L with an average concentration of 269 µg/L. BPA concentration in effluent is considerably lower than in the influent indicating that the level in both leachates and wastewater can be reduced after a treatment process, but the contamination is constantly replenished faster than the removal rate.

Yamamoto et al. (2001) found the concentration of BPA in samples from four different landfill leachates to range from 15 – 5,400 µg/L before treatment and 0.5 – 5.1 µg/L in the treated effluents (Yamamoto et al., 2001).

Contamination of BPA in the environment can also affect aquatic species. As seen from the literature (Kinch et al., 2015). Globally, BPA is the most abundantly detected phenolic compound in surface waters globally. Aside from its occurrence in water bodies, studies have shown that BPA bio accumulates in the meat of freshwater and seawater fish (Wei et al., 2011; Kinch et al., 2015). Fish is an important human food product. It is also at the top of the aquatic ecosystem food chain. Fish and other aquatic species living in contaminated water ingest BPA. Consequently, humans can be exposed to BPA through the consumption of aquatic food products (Kinch et al., 2015).

## **2.6.5 Fate of BPA in the Environment**

Various biotic and abiotic processes act to degrade and remove BPA upon discharge into the environment. Apart from its solubility in the environment, BPA is also prone to adhere to suspended solids and sediment, and is perhaps subject to photodegradation. Furthermore, BPA can be biodegraded by microorganisms present in the environment and metabolized by enzymes in plants and animals. BPA is not expected to substantially hydrolyse and volatilize in the aquatic environment (Staple, et al., 1998).

### **2.6.5.1 Biodegradation**

Several bacteria have been identified in soils, surface waters and in wastewater treatment plants as capable of biodegrading BPA, but with differences in the removal rate (Fürhacker

et al., 2000). In surface water and wastewater treatment plants aerobic biodegradation is important in BPA removal. This process occurs mainly in oxygen rich waters. Limited bacteria with high ability to degrade BPA have been identified. Two different strains including the *Pseudomonas sp* and *Pseudomonas putida* strain have been identified to show high BPA biodegradability (up to 90%). Also, a *Streptomyces sp.* strain isolated from river water showed a capacity to enhance BPA biodegradability, but with less than 90% for 10days. These bacteria with high ability to degrade BPA may be helpful for the purification of BPA contaminated aquatic environment. Regardless of BPA degradation in the surface water by bacteria, the half – lives (3-5days) may be long enough to have an impact on aquatic organisms. Furthermore, there is a major difference in BPA biodegradation under aerobic and anaerobic conditions. Under anaerobic conditions, BPA is not biodegraded. Studies with spiked samples shows that BPA biodegrades rapidly (above 90%) under aerobic conditions, but biodegradation was hardly observed under anaerobic conditions (less than 10% for 10 days) (Kang & Kondo, 2006). Wastewater treatment plants use bacteria to remove BPA from wastewater. Different studies have shown that up to 90% of BPA can be successfully removed in the wastewater treatment process (between influent and effluent) (Staple et al., 1998). However, effluents containing BPA can be a source of BPA in the aquatic environment.

#### **2.5.5.2 Toxicity**

In October 18, 2008, the Canadian Government released a final evaluation of BPA and the accompanying risk-management scope document. BPA has been listed toxic under the Canadian Environmental Protection Act for possible negative impacts on both human health and ecosystems. BPA is a compound with a very high estrogenic potential with confirmed to have endocrine disruptive effects in humans and other higher life forms at very low concentrations. The significances of such disruptions can be profound due to the importance of hormones in regulating living organism's growth and development. The effects of low BPA doses have been reported in experimental animals and human. In the United States, very low doses of BPA were stated to cause cardiovascular disease, liver enzyme abnormalities, type 2 diabetes and proliferation of human prostate cancer cells in a representative sample of the adult population (Teeguarden & Hanson-Drury, 2013).

#### **2.7 Analytical methods**

Emerging contaminants are increasingly detected in aqueous samples. Pharmaceuticals, industrial chemicals and related compounds encompass a large group of compounds of many different classes, including parent compounds and their degradation products (metabolites). There is growing concern about the use of these compounds. As mentioned, trace level quantities have been detected in the aquatic environment. There have been challenges in the analysis of these contaminants due to their polarity, thermal lability, the complexity of their chemical properties, matrix complexity and low concentrations in the environment (Petrovic et al., 2003). Therefore, the extraction technique, sample volume and analytical instrument used depend on the properties/behaviour of compounds to be analysed and the source of the water sample. For example, the analysis of WWTP effluents provides notable challenges for trace quantification due to the presence of several other interfering compounds related to organic matter in the effluents. Consequently, the investigation of the occurrence of these compounds requires extensive extraction, clean up and both selective and sensitive instrumentation. With developments in technology, there has been improvement in the analysis of trace chemicals in samples in aqueous state. Different studies have focused on the techniques for the detection and quantification of these contaminants in the environment (Radjenovic et al., 2007; Basaglia, 2011; Anumol et al., 2013). Different methods have been used in order to increase the accuracy of analysis (Kasprzyk-Hordern et al., 2008; Busch, 2009; Basaglia, 2011). Analysis of emerging contaminants in different environmental matrices is predominantly based on chromatographic separations and mass spectrometric detection. Prior instrumental analysis, various sample pre-treatment stages including filtration, pH adjustment, extraction and sample concentration are commonly required.

Generally, a good sampling practice, conserving sample transportation, suitable sample extraction, and the use of suitable analytical instruments are very essential to attaining accurate quantitative and qualitative analysis data (Jernberg, 2013). Several analytical techniques have been developed and optimized for analysis of various groups of ECs (González-Barreiro et al., 2006; Anumol et al., 2013). Lately, multi-residue techniques have also been introduced for the simultaneous analysis of a wide group of ECs with differences in physicochemical properties, e.g. water solubility, and log K<sub>ow</sub> (Anumol et al., 2013). This technique is convenient, because it reduces the total analysis time, and experiment cost. Accessibility of a multi-residual analytical method that allows measurement at a very low (ng/L) level has been highlighted as the basic need for accurate risk assessment and

monitoring of surface waste and drinking water quality (Petrović et al., 2003). Below is a brief review on the analysis of ECs in aqueous samples.

### 2.7.1 Sample Preparation

Firstly, filtration (especially for wastewater) is recommended, because samples with high loads of organic and suspended matter can obstruct the performance of the subsequent extraction step. However, some target compounds may be removed along with the suspended particles, therefore, washing the filters with suitable solvents after filtration is suggested (Wille et al., 2012). This stage also includes the extraction and clean up step. Sample extraction involves the transfer of the analytes of interest from a complex matrix to a simple solution and purifying extracts to minimise or eliminate mass interference co-eluted with analytes prior to instrumental analysis.

Several sample preparation methods are available for extraction and concentration of contaminants aqueous sample. Solid phase extraction (SPE) and liquid–liquid extraction (LLE) techniques have been predominantly used for extraction, but also some other techniques like stir bar sorptive extraction (SBSE) and solid phase microextraction (SPME) can be applied.

**Table 2.5: Procedural steps used in sample preparation techniques**

LLE	SPE	SPME
Addition of organic solvents to the sample	cartridges or membranes Conditioning	Exposing SPME fibre to the sample
Vigorous shaking of the sample	Sample loading	Analytes desorption in Solvent
Separation of aqueous and organic phases	washing to remove interferences and analyte Desorption	Injection in the analytical Instrument
collection of organic phase	Analyte elution	
Evaporation/concentration of the organic phase	Evaporation / concentration of the organic phase	
Injection in the analytical Instrument	Injection in the analytical Instrument	

The basic operating principle of any sample extraction technique is to allow analytes to partition between sample matrix and an extraction phase.

Although the application of SBSE and SPME is increasing, they are still limited because of the requirements of some specific instrument accessories (Subramanian et al., 2011). Table 2.5, above shows major steps followed during different aqueous sample preparation methods such as LLE, SPE and SPME. Lately, solid phase extraction (SPE) is the most frequently used method of extraction and has replaced the liquid- liquid extraction (LLE) technique. LLE is time consuming, labour intensive, and requires the use of toxic solvents. The length of the experimental procedure involved with LLE often results in loss of analytes, thereby making the sample preparation stage the main source of errors in the analysis. This study focuses on SPE technique.

### **2.7.2 Solid Phase Extraction Technique**

SPE has emerged as a productive technique since its development in the 1980s for compound isolation and purification. Unlike other extraction techniques, sample isolation, concentration and clean up can be carried out simultaneously with SPE. Also, many difficulties associated with LLE can be averted; including incomplete phase separation, poor quantitative recoveries, and the use and final disposal of large quantities of solvent. In solid phase extraction, analytes are adsorbed onto the solid phase sorbent. The sorbent is washed with solution to eliminate unwanted compounds co-eluted with the target analytes prior to analytes elution. A general SPE analytical method for aqueous environmental samples involves the use of octadecyl (C18) silica, polymeric, or hydrophilic - lipophilic balance (HLB) with either disk or the frequently used cartridges. Extraction of ECs using SPE has been improved by developing a different polymeric sorbent, which is typically hydrophilic-lipophilic in nature. Oasis HLB, which is a copolymer of divinylbenzene and vinylpyrrolidone, is presently the most frequently used SPE sorbent for multi-residual ECs extraction. HLB has been specified to give better results at neutral sample pH. With C18, there is a need for sample pH alteration, which depends on the nature of the target analytes.

Other copolymer cartridges used include Isolute ENV+, chromobond HR-X and Strata-X (Jernberg, 2013). After extraction, analytes are collected from the sorbent by elution with pure polar solvent, commonly acetonitrile or methanol. SPE has commonly been achieved before separation and detection of pharmaceuticals (off- line SPE). Lately, on-line SPE has also been proven an effective extraction technique. On-line SPE is coupled directly with an

analysing system (e.g. LC/MS) or may be used as a fully automated system (Wille et al., 2012).

Anumol et al. (2013) applied SPE (HLB cartridges) for the simultaneous extraction of 36 trace organic contaminants including pharmaceuticals, pesticides, industrial chemicals e.g. bisphenol A, polyfluorinated compounds (PFCs), steroid hormones and personal care products in wastewater, surface water, groundwater and drinking water. Good recoveries of 90-110%, 39-121% and 38-141% were reported in ultrapure water, surface water and wastewater respectively.

For PFC analysis, different extraction techniques have been investigated due to variation in their polarity. Weak anion exchange (WAX) SPE cartridge and methanol and acetonitrile have been used for extracting the ionic, water soluble short-chain perfluoroalkyl sulfonates (PFOS) and perfluoroalkyl carboxylates (PFCAs; C<sub>4</sub>-C<sub>6</sub>), while the purely hydrophobic (C18) or the hydrophilic-lipophilic balance (e.g. Oasis HLB) cartridge can be used for less polar and long chain PFCs (van Leeuwen & de Boer, 2010). Taniyasu et al., (2005) compared weak anion exchange (WAX) and HLB cartridge for the extraction of perfluorochemicals. Recoveries with HLB cartridge were generally >80%, except for the short chain perfluoroalkylcarboxylates such as perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA) and perfluorobutyric acid (PFBA) whose recoveries were less than 30%. Short chain perfluoroalkylcarboxylates were excellently trapped by WAX cartridge with good recoveries between 85 and 107%. To determine the contaminants at trace level in environmental samples, pre-concentration is generally necessary prior to chromatographic detection (Zhao et al., 2007). Figure 2.7 below shows a typical commercially available SPE cartridge.

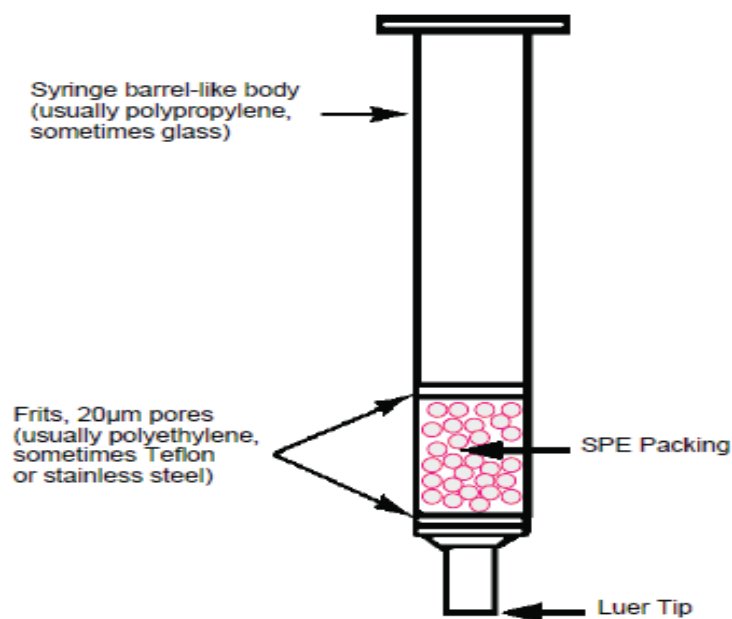


Figure 2.7: A typical SPE cartridge (Basaglia, 2011)

### 2.7.3 Compound Determination

Gas (GC) chromatography and Liquid chromatograph (LC) are the two most important techniques used for the analysis of pharmaceuticals and other emerging compounds in different environmental matrices. Chromatography is a separation method, which is based on the interaction of an analyte between the stationary phase and the mobile phase. Analytes with differing tendencies to interaction with the phases travel through the chromatographic system over different lengths of time. Due to its versatility, high specificity and selectivity, LC-MS/MS has become the preferable analytical technique. It is used in the analysis of non-volatile thermolabile compounds with wide ranges in polarity. This method is increasingly replacing GC-MS and LC-MS. Occurrence of matrix effects is the major negative aspect for LC analysis of pharmaceuticals and other emerging contaminants in environmental matrices (Wille et al., 2012). Nevertheless, GC coupled with detectors such as FID and MS can be effectively applied for volatile and semivolatile non-polar compounds. The major disadvantage attributed to the GC technique is the time-consuming derivatization step, which can increase the risk of analyte loss. Similarly, errors may also be introduced into the analytical procedure during this step (Kolpin et al., 2002). Until the end of 1990s, trials to develop instrumental methods for determination of PFCs were hindered due to the absence

of chromophores and their non-volatile nature. GC-MS after sample derivatization has been applied to determine perfluoroalkyl carboxylates (PFCAs). GC-MS cannot effectively analyse perfluoroalkyl sulphonates due to their inability to form stable volatile derivative (González-Barreiro et al., 2006). Therefore, other techniques such as LC will be considered.

Most analytical methods of PFC determination is based on liquid chromatography coupled to mass spectrometry or tandem mass spectrometry and interfaced with an electrospray ionization source (LC-ESI-MS) in negative mode (Hansen et al., 2001; Tseng et al., 2006) and LC coupled to ESI time-of-flight mass spectrometry (LC/ESI-TOF-MS) (Vanhaecke et al., 2010). Matrix effects (ionization suppression or enhancement in the electrospray) have been a major problem in the PFCs quantification using LC/MS/MS. Different methods of sample preparation have been employed to overcome matrix effects.

#### **2.7.4 Analysis of emerging contaminants with LC**

Liquid chromatography (LC) is widely applied for the analysis of water samples as the analytical procedure can be automated and the analytes of interest can be determined directly in an easy and time-saving operation. Recently, reversed phase liquid chromatography (RP - LC) is applied more for the analysis of emerging contaminants (bisphenol A, acetaminophen and PFCs). Reversed phase show column efficiency, higher stability and versatility with several mobile phases of different compositions for the application of varieties of compounds. This technique involves the use of non-polar organic stationary phase column-packed materials (such as octyl - C8 or octadecyl- C18 and dimethyl- polymeric materials) and polar aqueous mobile phase including acetonitrile, methanol, isopropylalcohol, ethanol, acetone, etc. The choice of mobile phase composition solely depends on the polarity of the analytes of interest. Furthermore, solvent miscibility and solvent-analytes interaction during LC method optimization must be considered. In a brief explanation of RP principle, non polar/hydrophobic compounds in the mobile phase are easily attracted to and tend to bond to the non-polar hydrophobic stationery phase. Consequently, polar/hydrophilic compounds are eluted first, followed by less polar and non-polar or weakly polar compounds in the end (Nurmi & Pellinen, 2011).

Due to the presence of many emerging contaminants in trace quantities ( $\mu\text{g/L}$  or  $\text{ng/L}$  levels) in the environment, conventional detection methods, such as ultra violet-visible (UV/Vis) detection and fluorescence detection, cannot meet the needs for their detection in aqueous samples. MS coupled with other separation techniques has been widely used for quantitative

and qualitative analysis of emerging contaminants in water samples. Furthermore, LC/MS/MS with different ionization interfaces - electrospray (ESI) and atmospheric pressure chemical ionization (APCI) - has been applied for the analysis of various emerging contaminants in water samples. Electrospray ionization is frequently used to convert the analyte of interest into a single ion for mass spectrometer detection. Tandem mass spectrometry involves multiple steps of mass selection for the detection of analyte ions and it involves the quantification of ions in selective ion monitoring (SIM) and multiple reaction monitoring (MRM) modes, which increases the specificity of detection. Other detectors used include quadrupole-time of flight (QqToF), triple quadrupole (QqQ), and quadrupole-linear ion trap (QqLIT) (Mastroianni et al., 2011).

Occurrence of matrix effects is the major set back attributed to HPLC technique for pharmaceuticals and other emerging contaminants analysis in environmental matrices (Wille, et al., 2012). Presently, ultra-performance liquid chromatography (UPLC) and ultra-high-performance liquid chromatography (UHPLC) have been introduced (Kasprzyk-Hordern et al., 2008). These analytical instruments are capable of operating at very high pressures (>1000 bar). UHPLC uses columns with sub-2- $\mu\text{m}$  particle diameter, which tolerates faster separation of compounds, increased sensitivity, better resolution and reduced matrix effects than conventional HPLC (Jernberg 2013). LC can be coupled to a MS detector with different ionization interfaces; electrospray (ESI) and atmospheric pressure chemical ionization (APCI) and detectors, such as quadrupole-time of flight (QqToF), triple quadrupole (QqQ), and quadrupole-linear ion trap (QqLIT) (Mastroianni et al., 2011). The most widely used ionization techniques are the ESI and APCI. They are ionization techniques, which generally produce protonated or deprotonated molecules.

From the preceding literature, it can be pointed that globally, there have been extensive occurrence of the studied ECs in wastewater, drinking water and aquatic environment. In South Africa, there is limited information on their presence in drinking water and aquatic environment and no study have been done in wastewater in the Western Cape.

## CHAPTER 3

### PLANT DESCRIPTION AND METHODOLOGY

#### 3.1 Introduction

To date, several analytical methods have been developed and applied for the determination of emerging contaminants. However, quantification of low concentrations (ng/L to µg/L) is one of the major challenges in the analysis of ECs (Petrovic, Gonzalez & Barcelo, 2003). This chapter describes the experimental procedure used in this study, which includes reagents, chemical standards, and analytical techniques. This chapter also describes the field study sites, including the sampling procedures used, different treatment methods available in the studied WWTP and sampled points. Validation of the methods used to determine the compounds of interest in this study is also described. Furthermore, analytical methods for water quality parameters such as pH, temperature, electrical conductivity, and total dissolved solids, nitrogen, orthophosphate, total organic carbon (TOC) and chemical oxygen demand (COD) are described.

#### 3.2 Description of WWTPs

Samples were taken from four different WWTPs in and around Cape Town, South Africa over a period of four months (February – May 2015) when entries to the WWTPs were given without restrictions. All samples were collected in triplicate. The WWTPs include, Beaufort West water reclamation plant, Bellville WWTP, Zandvliet WWTP and Scottsdene WWTP. A summary of the WWTPs is given in Table 3.1.

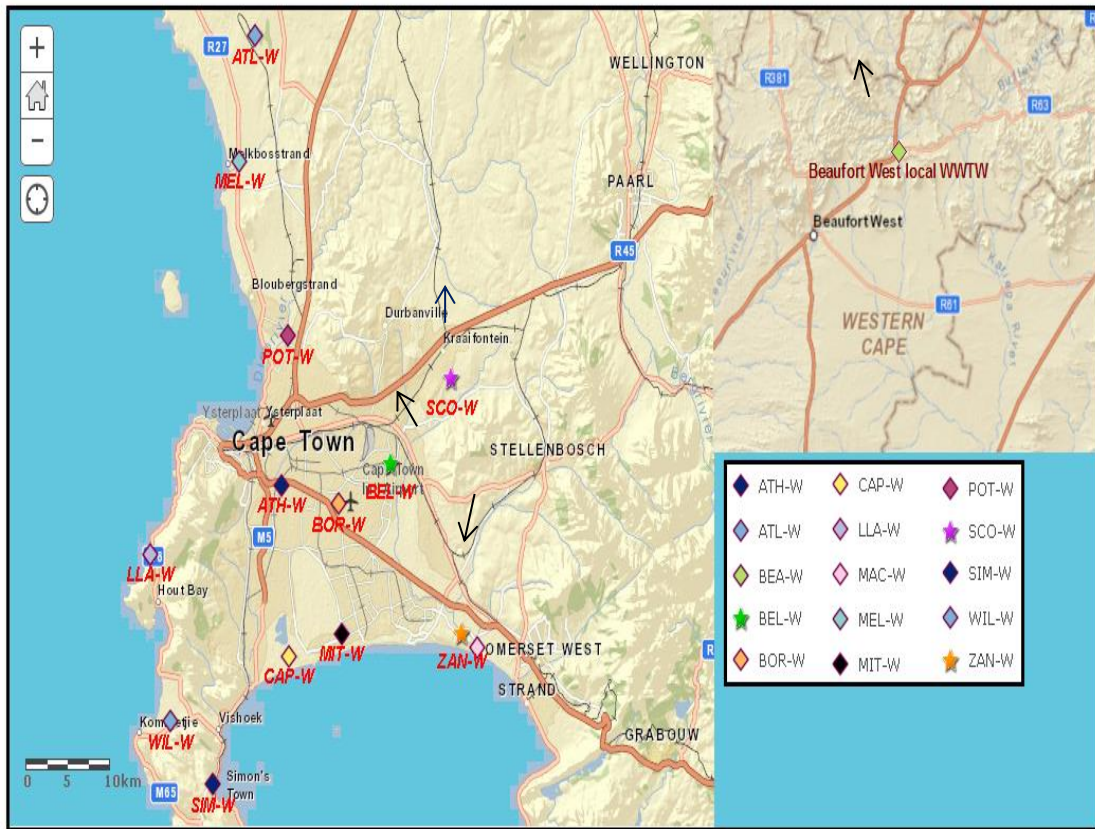


Figure 3.1: Wastewater treatment plants in the Western Cape. (Drafted by Oluseyi Abegunde (PhD student, Applied geology, University of the Western Cape, South Africa)

Map showing BEL-W: Bellville wastewater treatment plant, ZAN-W: Zandvielt wastewater treatment plant, SCO-W: Scottsdene wastewater treatment plant and Beaufort West wastewater reclamation plant

### 3.2.1 Beaufort West WWTP

This WWTP serving a population of 45,000 is the South Africa's first direct wastewater reclamation plant for potable water production. The first treatment stage includes screening and grit removal, followed by secondary treatment, which includes treatment with activated sludge, chlorination and dosing with ferric chloride ( $\text{FeCl}_2$ ) to increase phosphate removal efficiency as well as settling as to prevent algae growth and membrane blockage. Treated wastewater effluent is conveyed directly to a water treatment facility for further treatment to meet drinking water standards. The water reclamation plant process includes the use of combined secondary treatment (activated sludge process), sedimentation basin, pre-chlorination stage and a multiple-barrier treatment approach, such as rapid sand filtration, ultrafiltration, reverse osmosis (see Figure 3.2), UV-hydrogen peroxide and final chlorination stage. Beaufort West WWTP receives inflow from commercial and domestic

effluents and it contains no known industrial effluents. Figure 3.3 also shows the conceptual process diagram of Beaufort west WWTP.



Figure 3.2: Membrane system at the Beaufort west WWTP. (a) Reverse osmosis, and (b) ultrafiltration (Ivarsson & Olander, 2011)

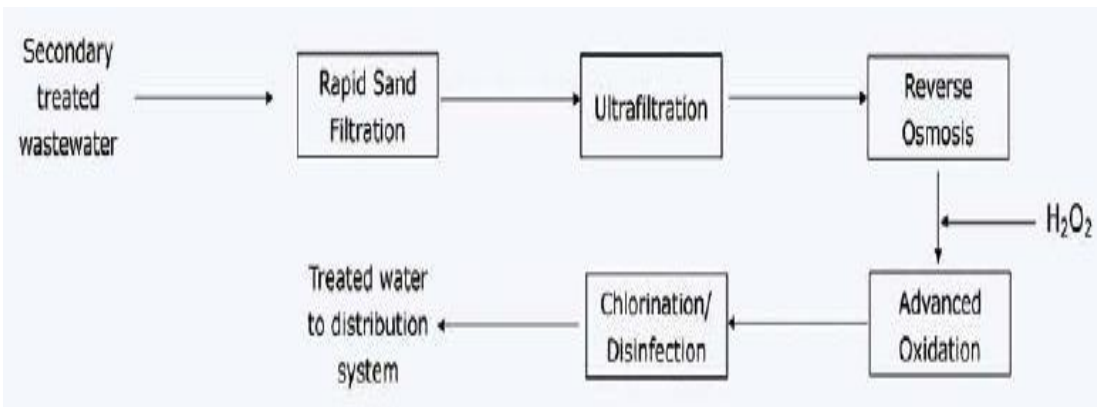


Figure 3.3: Conceptual process diagram of Beaufort West WWTP (Ivarsson & Olander, 2011).

In Beaufort West WWTP, samples were taken at the WWTP inflow and at different stages of treatment: WWTP, secondary treatment process (after activated sludge and chlorination),

tertiary treatment process, AOP (after ultrafiltration, reverse osmosis, and UV/H<sub>2</sub>O<sub>2</sub>) and the final effluent.

### **3.2.2 Zandvliet WWTP**

The WWTP serves over 400,000 people with a total capacity of 77 MI/day. The plant inflow sources mainly municipal and commercial. Inflow is from the residence of Khayelitsha and Blue downs. The available treatment process consists of preliminary treatment stage (screening and grit removal), an activated sludge (AS) system, membrane bioreactor (MBR) treatment stage and chlorination stage. The final effluent is discharged into Kuils River. Samples were taken from the plant influent, after AS treatment, after MBR treatment and at the effluent.

### **3.2.3 Bellville WWTP**

Bellville WWTP has an average capacity of 54.6 MI/day and it serves a population of about 591,000. The plant receives mainly industrial effluent and some quantities of municipal, commercial and institutional wastewater from the northern suburbs of Cape Town as well as landfill leachate from the nearby landfill site. The plant operates primary treatment, an activated sludge process with anaerobic, anoxic and aerobic treatment, secondary sedimentation, a separate MBR treatment and chlorination. The plant effluent is applied for industrial reuse, irrigation and some portions are discharged into Kuils River. Access was given to all the treatment stages for sampling except the MBR section.

### **3.2.4 Scottsdene WWTP**

The Scottsdene WWTP is a small sewage treatment facility with a present treatment capacity of 12.5 MI/day. The treatment plant receives wastewater from the urban areas of Scottsdene, Wallacedene, Kraaifontein and a small light industrial area. The WWTP serves a population of about 92,700 and the service area covers approximately 350 hectares. Scottsdene treatment process includes screening, grit removal, activated sludge process, extended aeration and disinfection by chlorination. The final treated effluent from the Scottsdene WWTP is usually discharged into the dam downstream and Bottelary River, from which water is used for farming purposes. Permission was only granted for influent and treated effluent sampling. Below is the summary of the treatment processes in the studied plants.

**Table 3.1: Summary of treatment processes in the studied WWTPs**

<b>WWTP</b>	<b>Primary Treatment</b>	<b>Secondary Treatment</b>	<b>Tertiary Treatment process</b>	<b>Advance Oxidation process</b>	<b>Average flow (Ml/d)</b>	<b>Population Equivalent</b>
<b>Beaufort West</b>	Screening, grit removal and sedimentation	Activated sludge, and secondary settling	Pre-chlorination, rapid sand filtration, ultrafiltration, and reverse osmosis	UV/H <sub>2</sub> O <sub>2</sub> and Final chlorination	4.6	41,000
<b>Zandvliet</b>	Screening, and grit removal	Activated sludge and membrane bioreactor	Chlorination	---	85	460,000
<b>Bellville</b>	Screening, grit removal	Activated sludge, extended aeration	Sedimentation	UV disinfection	54.6	591,000
<b>Scottsdene</b>	Screening, grit removal	Activated sludge, extended aeration	Sedimentation	Chlorination	12.5	92,700

### **3.3 MATERIALS AND METHOD**

#### **3.3.1 Labware**

The following equipment was used: 1L amber bottles, pipettes, measuring cylinder, polypropylene tube, 500 mg, 6cc Oasis HLB SPE cartridge (waters, South Africa), Strata X 500 mg (Phenomenex), beakers, 2 mL amber screw-caps septum vials, centrifuge, vacuum manifold and pump (VAC ELUT SPS 24 Port Agilent Varian, USA), and 0.45 µm filter papers (GF/A, Whatman, UK). All sample bottles, extraction, and volumetric flasks used were washed in methanol, rinsed well with tap water and lastly with de-ionised water prior to drying. The sample bottles were then air-dried.

#### **3.3.2 Reagents**

Methanol and acetonitrile purchased were HPLC grade. The following list of standards was purchased: perfluorooctanoic acid (PFOS 96%), perfluoroheptanoic acid (PFHpA 99%), perfluorooctanesulfonate (PFOS); (100 µg/mL in methanol), perfluorononanoic acid (PFNA 97%), perfluorodecanoic acid (PFDA 98%), perfluoroundecanoic acid (PFUnDA 95%), bisphenol A (≥99%) and acetaminophen (≥99%) from Sigma Aldrich (South Africa). Water was purified by Milli-Q system (Millipore, Bedford, MA, USA).

#### **3.3.3 Solutions**

Primary stock solutions of individual analytes were prepared in methanol at a concentration of 1000 µg/mL. Working standard mixture solutions were prepared by appropriate dilution of the stock solutions in methanol. All solutions were stored at 4°C in amber glassware to prevent light degradation. Working standard solutions were used for preparation of the calibration curves and for spiking samples in the validation study.

#### **3.3.4 Sample Collection and Handling**

Triplicate samples were collected at each stage of the treatment process from the four different wastewater treatment plants. Samples were collected in pre-washed amber glass bottles with screw caps. Field blanks were also prepared by filling pre-washed bottles with ultrapure water, transported to the sampling site, subject to the sampled field conditions and transported back with the samples to the laboratory. Samples and field blanks were kept in the refrigerator at 4°C and analysed within 48 hours after sampling. Both ultrapure water

and wastewater samples collected from WWTPs were used for recovery and validation studies

### 3.3.5 Sample Preparation (Extraction and Clean-Up)

Oasis HLB was selected over Strata X cartridge for sample extraction after an optimization study using the two different reversed phase SPE columns. Samples were extracted in triplicate. Solid-phase extraction (SPE) was applied by using vacuum manifold. Up to twenty-four SPE (500 mg, 6 mL HLB) cartridges were connected to the manifold and the manifold was directly connected to a vacuum supply with tubes. Each cartridge was conditioned with 15 mL of methanol followed by 15 mL of -Q water, without allowing the water to drop below the top edge of the adsorbent packing material. The solid phase was kept wet for optimal extraction and to avoid cracking of the packing material. Wastewater samples (500 mL) were loaded in the pre-conditioned cartridge. The equipment flow rate was maintained at approximately 5 mL/min. Cartridges were washed with 5 mL of 40% methanol in water. This washing was discarded and cartridges were allowed to dry on the manifold under vacuum suction for 20 mins. Analytes were then eluted with 8mL methanol at a very low flow rate of 1 drop/sec.

At this stage, the vacuum pump was turned off to release the vacuum. The vacuum manifold was lifted up and a collection of pre-cleaned glass tubes were inserted into the rack to collect the extracts as they elute down the cartridges as shown in Figure 3.4. The extract was concentrated to 2 mL under a gentle nitrogen stream. Pre-concentration is necessary due to the small total concentration of analytes in various types of samples. The concentrated extracts was transferred to amber vials and centrifuged for 25 mins prior to analysis.

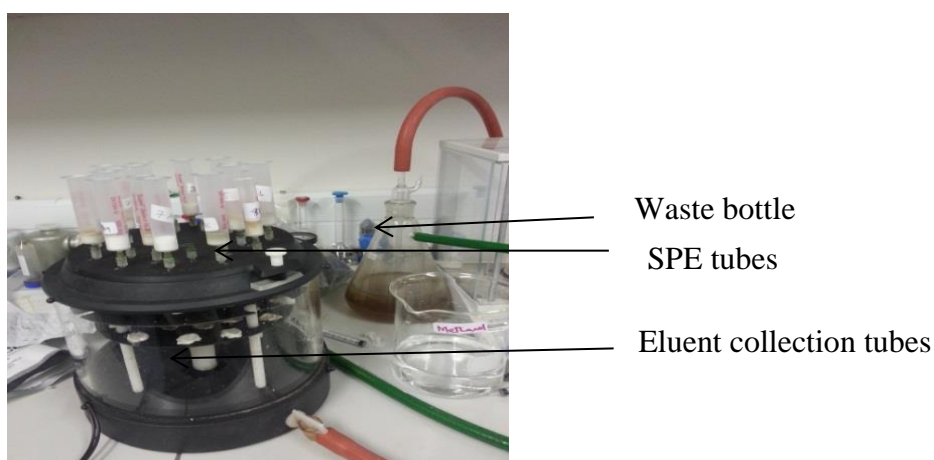


Figure 3.4: Varian vacuum manifold with SPE tubes, eluent collection tubes and waste bottle

### 3.3.5.1 Analytical characteristics of the methods

The analytical characteristics of the methods used are summarized in Figure 3.5. Individual standards for all analytes were prepared at concentrations ranging from 0.1 - 1000 ng/L (for all PFCs) and 50 – 2000ng/L (for bisphenol A and acetaminophen). The instrument limit of detection (LOD) for each analyte was determined by injecting standards on the UPLC/MS/MS system. Method precision was determined by replicate injection of standard mixtures of all analytes prepared in the laboratory. The LOD and limit of quantification (LOQ) were defined as the concentration for which the signal to noise ratio was greater than 3.3 and 10 respectively.

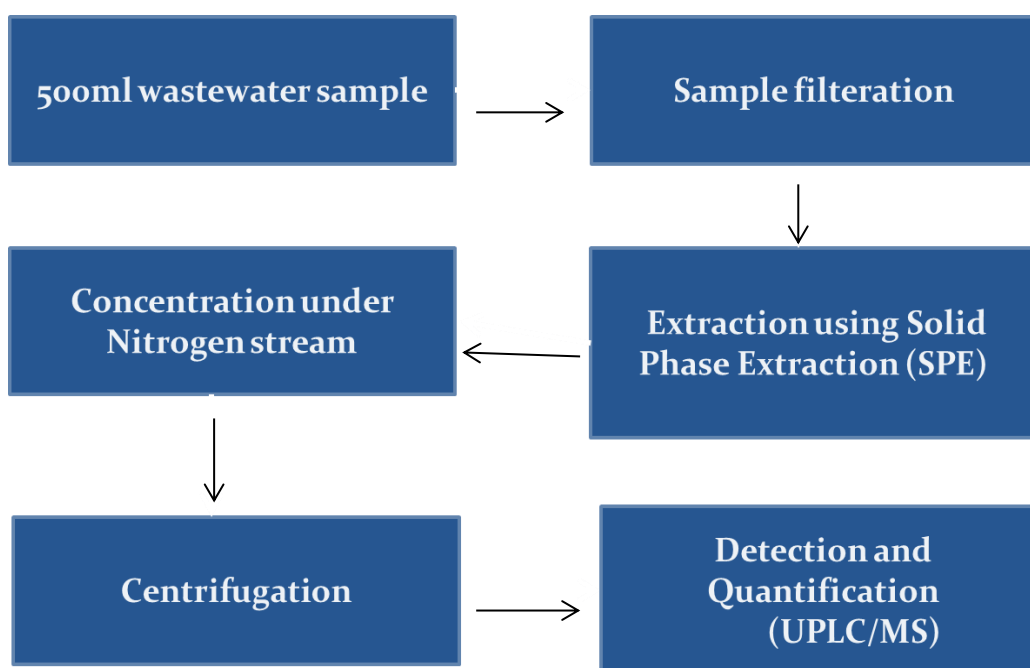


Figure 3.5: A schematic representation of the step-by-step analytical process

### 3.3.5.2 Sample analysis and calibration chromatographs

#### a) Chromatographic conditions

The chromatographic separations were performed with the ACQUITY UPLC™ (Waters). The instrument consists of ACQUITY UPLC binary solvent manager and ACQUITY UPLC sample manager.

Simultaneous determination of PFCs, Bisphenol A and acetaminophen was achieved using an ACQUITY UPLC BEH C18 1.7  $\mu\text{m}$  column (2.1 mm  $\times$  100 mm) with an ACQUITY BEH C18 1.7  $\mu\text{m}$  VanGuard™ precolumn (2.1 mm  $\times$  5 mm), supplied by Waters (Mildford, MA, USA). The column temperature was set to 50°C. The mobile phase consisted of a mixture of 2 mM ammonium acetate (solvent A) in mille-Q water and methanol (solvent B).

Linear gradient elution of 0.35 mL/min was used starting with a mixture of 80% solvent A and 20% solvent B for 9 min. At 10 min, the acetonitrile percentage was increased linearly from 90 to 100% and was later maintained at 80% solvent A and 20 % solvent B as shown in Table 3.2. A volume of 5  $\mu$ L of each sample was injected into the LC/MS system. Standards and the test samples were subjected to 12 min chromatographic run. Table 3.3 below summaries the analytical and instrumental condition used in this study.

#### **b) Mass spectrometry (MS)**

The UPLC was coupled to a triple quadrupole mass spectrometer (Xevo TQ-MS), with an electrospray ionization (ESI) source. During optimization, a multiple reaction monitoring (MRM) scan mode was generated for all analytes. In addition, for maximum sensitivity, other conditions such as source temperature, capillary voltage, cone voltage, cone gas flows and desolvation temperatures were optimized. This was achieved by direct injection of stock solutions with a concentration of 10  $\mu$ g/mL. The capillary voltage of 3.5 kV, desolvation gas (N<sub>2</sub>) flow of 800 L/h, source temperature of 120°C and desolvation temperature of 400°C were finally used. The whole analytical operation control and data processing were performed with Masslynx software.

**Table 3.2: Gradient elution method**

<b>Time(min)</b>	<b>Flow (mL/min)</b>	<b>%A</b>	<b>%B</b>	<b>Curve</b>
<b>Initial</b>	0.350	80	20.0	Initial
<b>9.00</b>	0.350	10.0	90.0	6
<b>10.00</b>	0.350	0.0	100.0	6
<b>10.10</b>	0.350	80.0	20.0	6
<b>12.00</b>	0.350	80.0	20.0	6

**Table 3.3: Summary instrumentation and analytical conditions**

<b>UPLC conditions</b>	
<b>LC System</b>	Aquity Ultra Performance LC (Waters)
<b>LC Column</b>	Aquity UPLC BEH C18 1.7 $\mu$ m (Waters)
<b>Column temperature</b>	50°C
<b>Eluent</b>	(A) 2 mM ammonium acetate in milli-Q water (B) 2 mM ammonium acetate in methanol
<b>MS condition</b>	
<b>MS System</b>	Xevo TQ-MS
<b>Ion Mode</b>	ESI+
<b>Desolvation Temperature</b>	400°C
<b>Desolvation gas (L/h)</b>	800
<b>R F lense (v)</b>	1.0
<b>Capillary Voltage (KV)</b>	3.5

### **3.3.6 Method modification, validation, quality control and calibration.**

The volume of each water sample used for the extraction technique was increased from 250 mL to 500 mL. To ascertain the concentration and consistency in the extraction technique for all the analytes, each extraction round was triplicated. To show the applicability of the analytical method, a validation study was carried out. The validation procedure included the assessment of method linearity, specificity/selectivity, precision, recovery, and calculation of the limits of detection (LODs) and quantification (LOQs). Six point calibration curves were constructed (four replicates). Also, to demonstrate the multi-matrix capacity of the analytical technique, an identical validation study was performed using ultrapure water and wastewater.

To monitor for potential laboratory contamination, blank samples of ultrapure water was extracted and analysed along with the field water samples and laboratory spikes. Methanol blanks were also run between samples in order to monitor for instrumental contamination

and carry over. Bisphenol A and acetaminophen were not detected in any batch of the blank samples. PFOA, PFDA and PFUnDA were detected at negligible levels in only one batch of the four batches of blank samples. Chromatographic peak area, signal noise and height were used to define the analytes of interest. For quantification, peak area was used to measure the optimal signal intensities. This provided the utmost reliable response amid the chromatographic response choices such as the peak height and the signal-to-noise ratio. Calibration standards were analysed prior to each analysis batch. The final analyte concentration was calculated as follows:

$$\text{Final analyte concentration} = \frac{\text{initial concentration} \times \text{sample volume injected}}{\text{Samples volume extracted}} \quad \dots (8)$$

### **3.3.7 Physicochemical Analysis of Wastewater Samples**

Some physicochemical parameters of wastewater from the different WWTPS were evaluated. For this purpose, water samples were collected in 1L plastic bottles with screw caps. Sample bottles were filled in a way that no air bubble was entrapped. Samples were transported in a cool box to the laboratory and were kept in the refrigerator at 4°C prior analysis. Samples holding time did not exceed 1 week. Both the on-site and laboratory procedures were clearly elucidated below.

#### **3.3.7.1 On site water analysis**

Parameters such as temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) of wastewater influent and effluent were measured at the sampling sites. Measurements were done with a portable multi parameter field meter (HANNA, HI 9811-5, USA). The field meter was checked and properly calibrated for each sampling.

#### **3.3.7.2 Laboratory water analysis**

The concentrations of total organic carbon (TOC), chemical oxygen demand (COD), orthophosphate ( $\text{PO}_4^{-3}$ ), and nitrite + nitrate as total N were determined according to methods specified in the relevant sections of this chapter. Methods for the analysis of each parameter are briefly described below.

#### **3.3.7.3 Chemical oxygen demand (reactor digestion method)**

COD analysis was carried out by the standard method described by EPA Method 410.4. To prevent contamination during analysis, all COD vials and screw caps were pre-washed with

20% H<sub>2</sub>SO<sub>4</sub> and were subsequently ignited in a muffle furnace at 500°C for one hour. 2.5 mL of each water sample was pipetted into COD vials. 1.5 mL of potassium dichromate (strong oxidizing agent) and 3.5 mL catalyst solution (sulphuric acid) were added vials were tightly capped and shaken to mix the layers together. Samples were placed into a COD reactor at 150°C for two hours. After two hours, vials were gently withdrawn and allowed to cool to room temperature. Samples were determined spectrophotometrically with a Hach DR/2010 spectrophotometer at the absorbance of 620 nm. COD values were calculated from the results of calibration standards, samples ID and absorbance (Andrew et al., 1995).

$$\text{COD as O}_2 \text{ mg/L} = \frac{\text{ABS} \times \text{slope}}{\text{V (mL)}} \dots\dots (9)$$

Where ABS = Absorbance and V is the volume of sample used

#### **3.3.7.4 Nitrate and nitrite analysis (flow injection analysis colorimetry)**

This analysis is based on US EPA, 1983 method 353.3 for analysis of water and wastewater. Firstly, sample pH was adjusted between 5 and 9. Samples were then filtered with 0.45 µm filter using a syringe. Filtered samples were injected each into LACHAT QuickChem® flow injection analyser (FIA) carrier stream at a flow rate of 2.5 µL/cm. The samples were moved through a QuikChem® 10-107-04-1-A copper-cadmium column for reagent preparation. This reduced the entire nitrate in the sample to nitrite. The reduced nitrate and nitrite (nitrate + nitrite as N) was then determined by diazotizing with 58.07 mM of sulphanilamide followed by coupling with 3.85 mM of N-(1-naphthyl) ethylenediamine dihydrochloride (Merck, Germany). Absorbance was measured at 520 nm with a colorimeter detector. Sample concentrations were computed by comparing sample absorbance with a standard curve. The data were moved from the omnion software as an excel sheet. Acceptable correlation coefficient of ≥ 0.999 was obtained. In house quality control samples and external proficiency testing (PT) samples were used for quality control (Andrew et al., 1995).

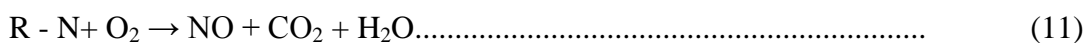
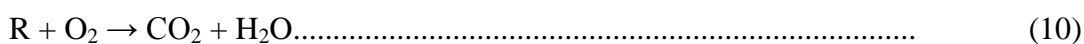
#### **3.3.7.5 Orthophosphate (method 8048 phosVer3/ascorbic acid method)**

Wastewater samples were diluted and treated with PhosVer3 reagent powder pillows. The orthophosphate ion (PO<sub>4</sub><sup>3-</sup>) reacted with ammonium molybdate and antimony potassium in an acid medium to form a mixed phosphate/molybdate complex. The complex formed was reduced with ascorbic acid, which later formed a molybdenum blue coloured complex. This

complex absorbed light at 880 nm. The absorbance is directly related to the orthophosphate concentration in the samples (Andrew et al., 1995)

### 3.3.7.6 Total organic carbon

Total organic carbon (TOC) is defined as all covalently bonded carbon in organic molecules and in surface and ground water, and organic carbon, which is not purgeable by acidification and gas stripping (Mohamed, 2011). In this study, TOC measurement was carried out according to standard methods for the examination of water and wastewater, using the high temperature combustion method 5310 B (APHA-AWWA-WPCF, 1989). Samples were acidified outside of the analyser with 2N HCl (pH 2) and the resulting CO<sub>2</sub> was purged, removing any inorganic carbon present in the samples. Afterwards the remaining carbon from the sample prepared in this manner was determined by combustion. The digestion was performed in the multi N/C 3100 by thermo catalytic high-temperature oxidation in the presence of a platinum catalyst. This enables a quantitative digestion even for very stable, complex carbon compounds. The sample aliquots were directly dosed into the hot zone of the filled reactor (combustion tube), while the pyrolysis and oxidation of the sample in the carrier gas flow were performed with the aid of the catalyst (the reaction equations are represented with equation 10, 11 and 12). The carrier was also used as an oxidizing agent.



Where R = carbonic substance.

The measuring gas was cooled in the condensation coil and condensed water was separated from the measuring gas in the subsequent total inorganic carbon (TIC) condensate container. After further drying and removal of corrosive gases, the measuring gas CO<sub>2</sub> was added to the NDIR detector. During this analysis, the total non-purgeable organic carbon content of the samples was detected (Andrew et al., 1995).

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Introduction

As previously discussed in Chapter 2, parameters such as physical and chemical parameters including biological, inorganic and organic substances describes the state of water/wastewater. This chapter firstly describes the results of the physicochemical parameters of the studied WWTPs influent and effluents. In addition, it presents the results obtained during the validation of the extraction methods, as well as, the analytical instrumentation used in the detection and quantification of the selected perfluorinated compounds, bisphenol A and acetaminophen. Furthermore, it presents the results and discussion of the target ECs.

#### 4.2 Water and wastewater quality parameters of the selected wastewater treatment plants

Interpretation of results is based on the DWA 2010 standardized levels for wastewater discharge, DWAF (1996) guidelines for domestic water use and SANS 241:2011 drinking water quality as well as some other water use guidelines in and outside South Africa.

**Table 3.4: Physicochemical Parameter Guideline Values in Drinking Water and Wastewater** (Government-Gazette, 1984; DWAF, 1996; DWA, 2010; SANS 241:2011, 2011)

Parameters, (unit)	South Africa		WHO	
	Wastewater	Drinking water	Wastewater	Drinking water
<b>pH (pH unit )</b>	5.5 - 9.5	5.5 - 7.5	6.0 - 8.5	6.0 - 8.5
<b>Electrical conductivity (mS/m)</b>	70 - 150	50 - 100		
<b>TDS (mg/l)</b>	450	≤ 1200	≤2000	
<b>Temperature (°C)</b>	≤ 25			
<b>Nitrate/Nitrite as N (mg/L)</b>	≤ 15	≤ 11.9		
<b>Orthophosphate as P (mg/L)</b>	≤ 10	≤ 1		
<b>COD (mg/L)</b>	≤ 75	≤ 30	≤ 1000	
<b>TOC (mg/L)</b>		≤10		

Only samples of the plants inflow and effluents were analysed for physicochemical parameters. The guideline limit based on the World Health Organization (WHO) and South African National Standards of selected water/wastewater parameters is presented in Table 3.4. The average concentrations of the water quality parameters detected in influents and effluents of the four studied WWTPs are shown in Appendix C

#### 4.2.1 pH and Temperature

Too high or low pH has been reported to have a toxic effect on aquatic species and can alter the solubility of chemical pollutants as well as some important elements such as selenium in the water bodies, thus causing negative effects on the ecosystem and humans (DWAF, 1996; Morrison et al., 2001). High temperature can affect the availability of oxygen in water.

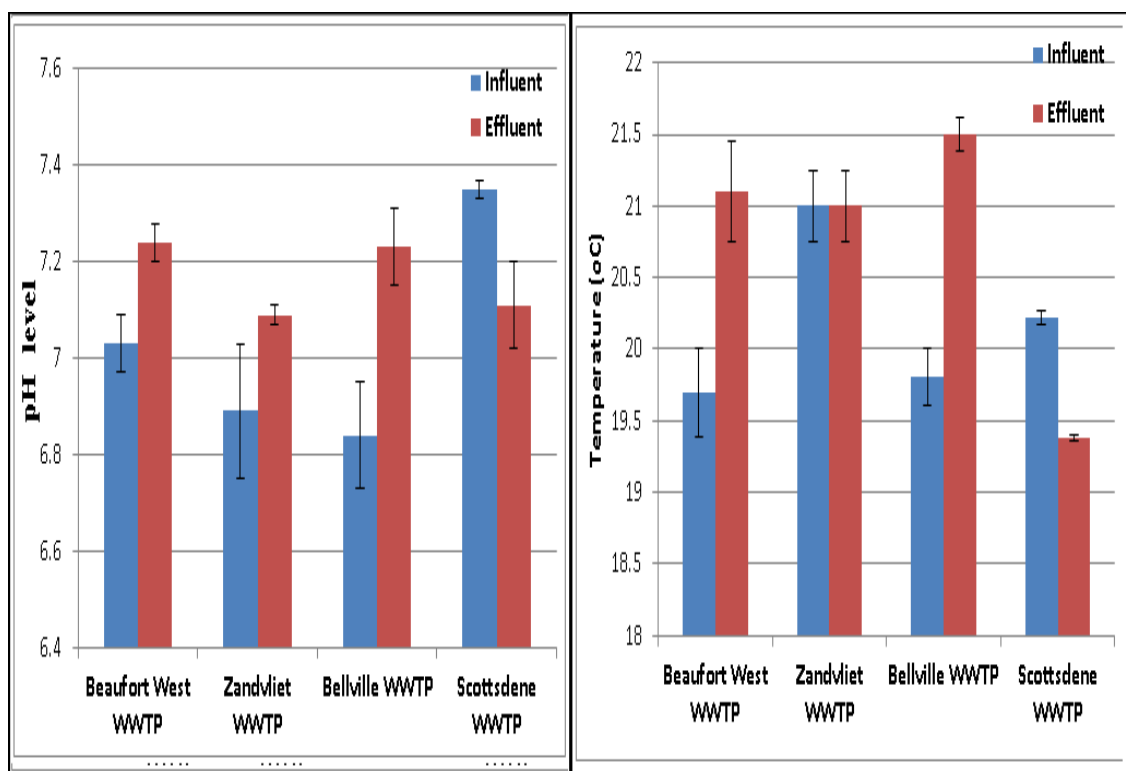


Figure 4.1: Presents pH and Temperature levels for influents and effluents of the wastewater treatment plants

It affects the toxicity of some elements such as Cu, Fe, Al, Mn in water bodies and increase the sensitivity of aquatic organisms to toxic substances (Akan et al., 2008; Odjadjare & Okoh, 2010). pH and temperatures level of wastewater influents and effluents from the four wastewater plants were analysed for, using portable multi parameter field meter (HANNA,

HI 9811-5, USA). Samples were analysed in replicates of three. The mean values of pH and temperature of wastewater influents and effluents are presented in the Figure 4.1.

The mean pH value for all the wastewater treatment plants ranged between 6.84 to 7.35 and 7.09 to 7.24 for influents and effluents respectively. Variation in the influent pH was observed in all the treatment plants, this might be due to the high variability in the quality of water treated in each plant. The lowest influent pH was observed in Bellville WWTP but the pH of effluent was similar to the pH values for the other WWTPs. However, there was an observable increase in effluent pH for all the WWTPs except the Scottsdale WWTP (see Figure 4.1). It can be deduced that the concentration of hydroxide ions ( $\text{OH}^-$ ) is increased during the wastewater treatment process. This evidently explains the sucking up of hydrogen ions in treatment systems. The pH values in both the influent and effluent in this study was lower than the observed pH in a study on industrial wastewater by Singh et al., (2012) in Dheradum, Uttarakhand, India. The pH values (as shown in Figure 4.1) for all the WWTPs are within the 5.0 – 9.5 range of the South African water quality limit for both effluent discharge and water reuse for domestic activities, as well as the 6.0 – 8.5 range specified by the World Health Organization guideline for wastewater effluent that is suitable for discharge into the environment (WHO, 2006), and the 6 - 9 pH range set as protection limit for aquatic life by the European Union. Thus, the obtained values suggest that the pH of the effluent may possibly not negatively affect the aquatic ecosystem.

The mean temperature ranged from 19.7°C - 21°C and 19.3°C - 21.5°C in the treatment plants influents and effluents respectively. There was an observed increase in the level of effluent temperature for Beaufort West and Bellville WWTPs and there was a slight decrease in the level of effluent temperature in both Zandvliet and Scottsdale WWTP. The overall effluent pH and temperature levels obtained in this study are similar to the results found by Odjadjare and Okoh, (2010) in an urban wastewater treatment plant in South Africa. The temperature values detected in the effluent were within the acceptable risk limit (see Figure 4.1) for South Africa domestic water use. In addition, this shows that the discharged effluent was of standard wastewater quality in terms of temperature.

#### **4.2.2 Total Dissolved Solid and Electrical Conductivity**

The electrical conductivity of water (EC) is an assay indicator of salinity. A high level of dissolved salts is often associated with wastewater effluents, especially from domestic sewage. The amount of total dissolved solids (TDS) are directly related to EC. TDS is

comprised of inorganic salts such as calcium, sodium, potassium, magnesium, chlorides, sulphate and bicarbonates dissolved in wastewater. High TDS and EC in wastewater treatment plant effluent can render water unsuitable for reuse by municipalities, agriculture (for irrigation), or for textile and paper manufacturing industries. Furthermore, high levels of TDS and EC in effluents increase the salinity of the receiving water bodies, thereby, causing adverse ecological effects on aquatic organisms (Morrison et al., 2001).

The level of the total dissolved solids and electrical conductivity level in wastewater influents and effluents from the four wastewater plants were analysed using a portable multi parameter field meter (HANNA, HI 9811-5, USA). Samples were analysed in replicates of three. The mean values of the total dissolved solids and electrical conductivity of wastewater influents and effluents are presented in the Figure 4.2.

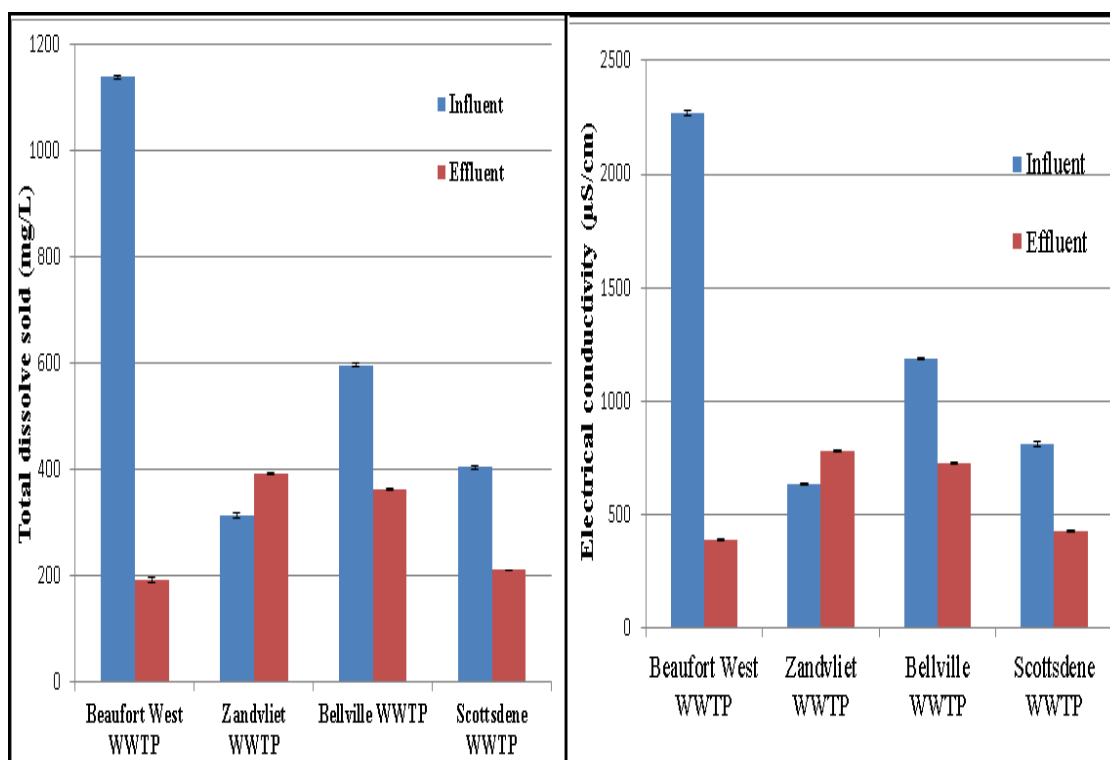


Figure 4.2: Electrical Conductivity and Total Dissolved Solid levels for influents and effluents of the wastewater treatment plants.

Figure 4.2 shows that the mean electrical conductivities (EC) of all the WWTPs influent ranged from 631 to 2271  $\mu\text{S}/\text{cm}$  and the final effluent ranged between 388 and 779  $\mu\text{S}/\text{cm}$ . The high EC values in the wastewater influent (especially in Beaufort West samples) are not surprising, because wastewater from domestic sources often contains high levels of dissolved salt (Singh & Bhatt, 2012). Higher EC levels in the effluents were found in this

study compared with the results from the study by Osode et al., (2009) on Dimbaza WWTP, Eastern Cape, South Africa. In Figure 4.2, it is shown that the level of EC was highly reduced from influents to effluent in Beaufort West (> 80%), and slightly removed in Bellville, and Scottsdene WWTPs (< 50%). Since EC is an indicator of total salt content, the low reduction (less than 50%) observed after the effluent treatment in both Bellville and Scottsdene can be explained in terms of the available treatment technologies (secondary treatments only) in these plants. It has been reported that salts such as potassium sulphate and sodium chloride escape through conventional water/ wastewater treatment plants and levels remain unaffected by treatment (Hammer, 1975; Morrison et al., 2001). In Zandvliet WWTP, a higher level of EC was observed in the final effluent compared to the plant inflow levels. This suggests that there could be other sources of pollution during the treatment process that could result in the increased values, or a high variability of EC in the intake water. In South Africa, the acceptable conductivity limit in domestic water supplies according to DWAF, 1996 is 70 mS/m or 700  $\mu$ S/cm and 170mS/m for drinking water according to SANS 241: 2011. Also the guideline value for electrical conductivity in effluent that could be released into the aquatic environment is 250 mS/m or 2500  $\mu$ S/cm (Government Gazette, 1984). The conductivity results obtained for all the four WWTPs indicates that the effluent quality for Beaufort West and Scottsdene treatment plants are compliant with the two above mentioned regulations for conductivity, while Bellville and Zandvliet treatment plants effluent quality appear non-compliant with EC limits in domestic water supplies. This suggests that Bellville and Zandvliet plant effluents are fit for discharge into aquatic environment, but are not fit for domestic reuse in terms of the EC values. High TDS concentration in water reduces the solubility of oxygen gas and increases the density of dissolved water (Bangash et al., 2006). The TDS levels in this study ranged from 315 – 1137 mg/L and 193 – 392 mg/L in the WWTPs influent and effluents respectively. The TDS concentration of all WWTPs decreased from influent to effluent. The highest TDS and EC in the influent was found in Beaufort West treatment plant and the lowest effluent values for these two parameters was observed in the same treatment plant (Beaufort West treatment plant) (see Figure 4.2). This indicates high performance of the treatment plants, especially with regard to the application of advanced treatment such as membrane process and reverse osmosis.

The effluent levels of the studied WWTPs are all within the acceptable limits of  $\leq 450$  mg/L,  $\leq 1200$  mg/L and  $\leq 2000$  mg/L for South African water uses (DWAF, 1996), SA drinking water guideline (SANS 241:2011) and WHO guidelines for effluent discharged into surface

water respectively (WHO, 2006; Akan et al., 2008). Akan et al., (2008) reported higher TDS values, ranging from 2210.21 – 2655.43 mg/L in Kano, Nigeria for the receiving watershed.

#### 4.2.3 Chemical Oxygen Demand (COD) and Total Organic carbon (TOC)

The level of the chemical oxygen demand (COD) and total organic carbon (TOC) of the wastewater influents and effluents from the four wastewater plants were analysed. The COD level was analysed based on the EPA Method 410.4 for water and wastewater analysis, which has previously been described in chapter 3 (section 3.3.7.3) of this study. Also the TOC level was analysed based on the high temperature combustion Method 5310 B (APHA-AWWA-WPCF, 1989) which has also been described in the same chapter 3 (section 3.3.7.6).

As previously discussed, COD is the measure of the amount of oxygen required to chemically and totally oxidise organic substances and mineral compounds to inorganic end products Mekibib, (2011). High levels of COD in water systems results in extreme oxygen depletion, which can adversely affect the aquatic species. The mean values of the COD and TOC of wastewater influents and effluents in this study are presented in the Figure 4.3.

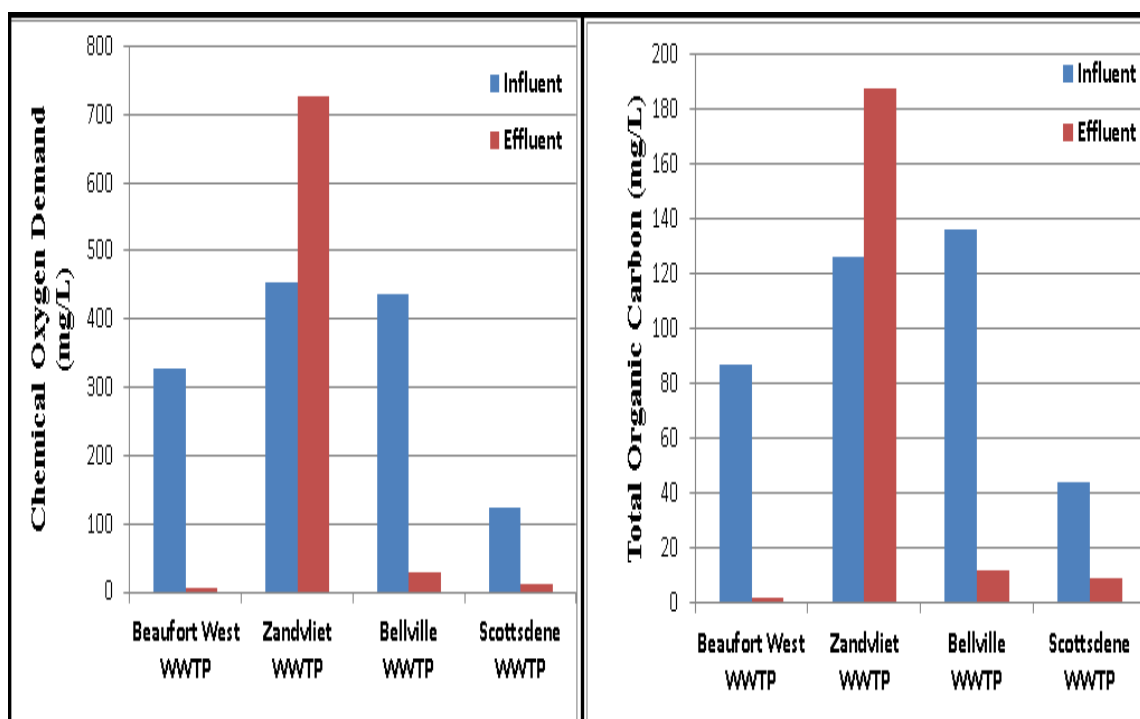


Figure 4.3: COD and TOC levels for influents and effluents of the wastewater treatment plants.

The chemical oxygen demand (COD) values in this study ranged from 124 mg/L to 454 mg/L in the influents and from 5 mg/L to 728 mg/L in the effluents (Figure 4.3). There was a distinct reduction in the COD values from influent to effluent for Beaufort West, Bellville, and Scottsdale WWTPs. Their effluent COD values were lower than the South African guidelines for COD ( $\leq 30$  mg/L) which can be discharged into the receiving aquatic environment (Government Gazette 1984). In Zandvliet WWTP, the observed COD value in the effluent was much higher than in the influent. This may be attributed to an increase in organic and inorganic matter, which might have been retained in the treatment plant or may be due to high variability of the influents/intake water. Although, Zandvliet effluent COD value (723 mg/L) is non-compliant with the 30 mg/L South African COD tolerance limit in wastewater effluent, the COD levels of all the four plants are still within the  $\leq 1000$  mg/L WHO guidelines limit for effluent that can be released into water bodies (WHO, 2006; Akan et al., 2008).

The TOC levels in this study ranged from 44 mg/L to 136 mg/L and 1.6 mg/L to 188 mg/L in the influent and effluent respectively of the four WWTPs investigated. TOC values for plants inflow were highest for Bellville (136 mg/L) followed by Zandvliet (126 mg/L), and then Beaufort West (87 mg/L). Very low TOC concentration compared to the other WWTPs was found in Scottsdale (9 mg/L). Generally, a distinguishable decrease in TOC concentration was observed in effluents for all the WWTPs except in Zandvliet where the concentration was greater than the influent. This variable decrease in TOC between plants shows that the pre-treatment methods applied in the treatment plants were not all equally effective in removal of the plant inflow TOC.

#### **4.2.4 Nitrate/Nitrite as N and Ortho-phosphate as P**

Nitrate, nitrite, and orthophosphate are nutrient sources, which can have an adverse effect on aquatic species at high concentrations. The level of nitrate/nitrite as N in the selected influents and effluents from the four wastewater plants was analysed based on US EPA, 1983 method 353.3 for analysis of water and wastewater as described in chapter 3 (section 3.3.7.4). The orthophosphate levels were analysed according to the PhosVer3/Ascorbic Acid Method (Standard method 8048 of water and wastewater analysis) as previously discussed in chapter 3 (section 3.3.7.5). Samples were analysed in replicates of three and the mean values of the influents and effluents are presented in Figure 4.4.

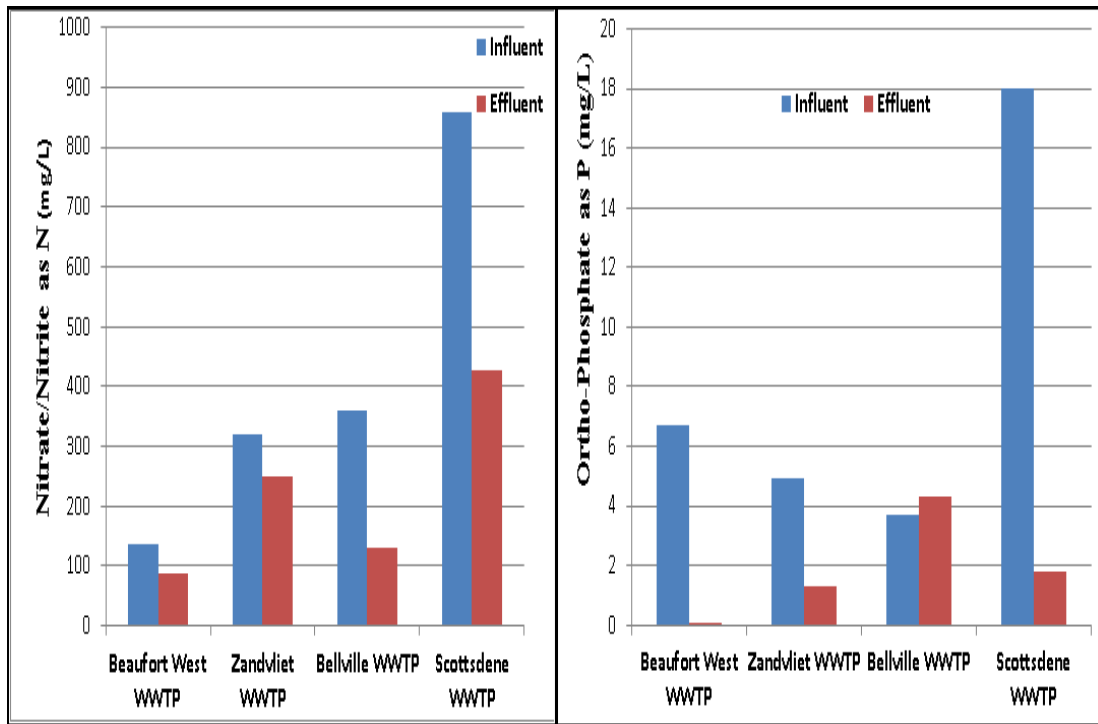


Figure 4.4: Levels of nitrate/nitrite as N, and Ortho-phosphate in the influents and effluents of the wastewater treatment plants.

Figure 4.4 shows that the mean value of nitrate/nitrite in the influent ranged from 137 – 856 mg/L, while the values for the effluents ranged from 87 – 428 mg/L. The highest value (859 mg/L) was observed in Scottsdale WWTP. This extremely high N value can be related to extensive agricultural activities in the area. High nitrate contamination can originate from agricultural sources such as runoff from animal wastes and farmlands using N-containing fertilizer. Very low removal efficiency (less than 50% in Beaufort West and Zandvliet WWTPs) was observed in all the WWTPs except in Bellville WWTP where 64% removal was observed. Igbinsosa et al., (2009) found lower values for nitrate and nitrite in treated final effluents in a studied WWTP in Eastern Cape Province of South Africa. Also, far lower values were obtained for total nitrogen (mean range from 2.90 - 6.90 mg/L) in a study by Momba et al., (2006) in WWTPs in Eastern Cape Province of South Africa. The South Africa guideline for nitrate in wastewater is 0.25 mg/L and 6 mg/L in domestic water. The WHO guideline value for nitrate in wastewater is 45 mg/L and the safe limit of 10 mg/L as N for life time use (WHO, 2006; Fatoki et al., 2003; Singh & Bhatt, 2012). Also, the South Africa general limit for nitrate/nitrite as N in wastewater is 15 mg/L (Government Gazette, 1984) and  $\leq 11.9$  mg/L in drinking water (SANS 24: 2011). Although there are limited or no available guidelines for nitrate/nitrite as N in wastewater globally, it is obvious that the N value found in all the four wastewater treatment plants is very high and exceeded regulatory

limits. Therefore, nitrate and nitrite can pose a problem to humans when the receiving water bodies are used for domestic purposes. Furthermore, relating the value found in Beaufort West treatment plant which is a water reclamation plant to the South African general limit for nitrate/nitrite as N in drinking water of 15 mg/L in drinking water, it can be concluded that this treatment plant does not comply with the guideline value in respect to nitrate/nitrite as N.

The orthophosphate levels in the WWTPs influent ranged from 3.7 – 18 mg/L, while the levels in effluent ranged from 0.05 – 4.3 mg/L. There was an observed decrease in the level from influent to effluent in all the treatment plants except in Bellville, where the level in the effluent appeared higher than in the influent. The orthophosphate effluent values observed in this study were lower than the reported values (3.4 – 7.5 mg/L) for Keiskammahoek sewage treatment plant, Eastern Cape, South Africa. In that study, the values reported for river water was similar to those in this study (Morrison et al., 2001). Generally, organic matter and nutrients such as N from treated or partially wastewater can stimulate physical, chemical and biological progression called eutrophication and cause increased algae growth when discharged into the aquatic environment (Igbinosa & Okoh, 2009).

#### **4.2.5 Summary**

Measurement of water/wastewater quality parameters and assessment of values for comparison with benchmarks such as guidelines and standards are used to evaluate water quality (Osuolale & Okoh, 2015). The results of the physicochemical analysis showed that seven out of the eight parameters analysed for in all the wastewater treatment plants complied with the South African (SA) effluent discharge standard limits as highlighted in DWAF and WHO guidelines. Although values were within discharge limits, the treatments did not always reduce the parameter showing high variability in the influents in the same time period and mostly the plants were not uniformly effective.

The parameters that are within the recommended limits were pH, TDS, EC, orthophosphates, temperature, COD (for the  $\leq 1000$  mg/L WHO guideline value) and TOC (only in Beaufort West and Scottsdene WWTPs). While nitrates/nitrites as N did not meet the SA set limits for effluent discharge and water reuse. Furthermore, all the parameters analysed (except nitrate/nitrite) for in Beaufort West wastewater treatment plant, which is also a water reclamation plant, complied with the DWAF (1996) guidelines for domestic water use and SANS 241:2011 guideline for drinking water.

### 4.3 Optimisation of the Extraction and Clean-Up Method

Prior to the extraction process for the selected compounds, a pre-filtration step was required for the influents due to the presence of suspended particles. Centrifugation was firstly attempted on each 500 mL sample at a relative centrifugal force (RCF) of 1500 x g for 20 minutes. This was compared to filtration of 500 mL of each influent sample using vacuum and filtered through Whatman filters (GF/A glass fibre filter). It was observed that the result of both methods yielded comparable background concentrations of the studied ECs present in the influent samples. Hence, filtration was preferred and chosen as the separation method due to the availability of filter paper, vacuum pump and because of the large volume of sample involved.

The extraction technique developed in this study was based on the modified method of Nurmi and Pellinen. (2011) and Anumol et al. (2013). Two types of commercially available reversed phase SPE cartridges; Oasis HLB (500 mg, 6 cc) and Strata X (500 mg, 6 mL) were tested with the intention of identifying and choosing the most appropriate reversed phase sorbent for extraction of the selected analytes. For this purpose, the two cartridges were tested on two different water matrices by spiking 1 mL of 10 µg/L of mixed standards of all the compounds of interest in 250 mL ultrapure water and wastewater. Spiked samples were extracted as described in chapter 3, using Oasis HLB and Strata X cartridges, and the final volume of extract was reconstituted to 1 mL. The choice of the SPE sorbent was primarily determined by the achieved recovery rates. The recoveries (extraction efficiencies) were determined using eight replicates and was calculated using the formula below:

$$\% \text{ Recovery} = \frac{\text{Concentration obtained}}{\text{Spiked concentration}} \times 100 \quad \dots\dots\dots (13)$$

The result of the recovery studies of all the analytes in wastewater samples and ultrapure water using Oasis HLB and Strata X cartridges is presented below in Figure 4.5.

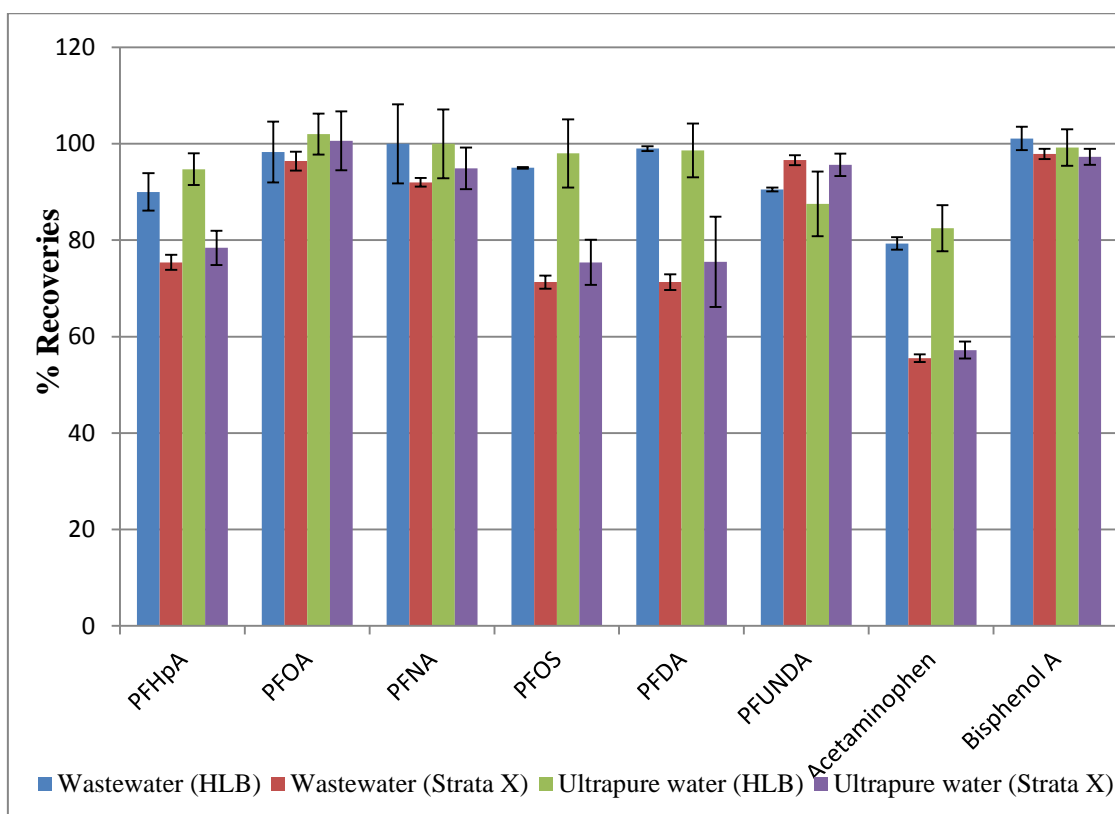


Figure 4.5: Percentage recoveries of the studied contaminants in both water matrices (ultrapure water and wastewater) using two different commercially available SPE cartridges.

The results in Figure 4.5 showed a wide range of 55.5% to 101.1% recoveries for all analytes. There may have been variations in the extraction efficiency of the analytes due to the difference in the interaction or affinity between the stationary phase of the polymeric SPE sorbents and each analyte. In addition, the high recovery (101%) of bisphenol A found in wastewater with HLB cartridge in this study can be due to procedural contamination during extraction the sample preparation. The overall result shows good recovery on the two tested reversed phase SPE columns. The similar recoveries achieved for all analytes are in agreement with the similar properties of sorbents. It can be concluded that the highest average recoveries for all analytes were achieved with Oasis HLB (as seen in Figure 4.5) when the two tested SPE sorbents were compared.

Simultaneous determination of six PFCs, bisphenol A and acetaminophen was investigated, using UPLC/MS/MS on an ACQUITY UPLC BEH C18 1.7  $\mu\text{m}$  column. Analytes were well separated under the previously mentioned conditions shown in Table 3.3 (chapter 3). At high flow rates, it was observed that the efficiency of UPLC columns of particle size  $<2.0 \mu\text{m}$  was not affected. Optimization of mobile phase was achieved by performing experiments on different mixtures of organic solvent and pH modifying buffer. In this study, the choice of

mobile phase was finally based on the peak resolution, peak shape and the sensitivity achieved for all the analytes. The gradients in both modes were also optimized after the mobile phase was selected. Several injection volumes were tested and 5 $\mu$ L was finally used as this volume gave the highest sensitivity without affecting the peak shape. The mass spectra were achieved by direct infusion of each standard in the mobile phase. ESI ionization source was used in both the negative and positive ionization mode. Detection of the negative precursor ion [M-H]<sup>-</sup> was carried out for PFCs and bisphenol A, while detection of the positive precursor ion [M+H]<sup>+</sup> was performed for acetaminophen. The individual Multiple Reaction Monitoring (MRM) parameters for the analytes are shown in Table 4.1 below.

**Table 3: Summary of the Multiple Reaction Monitoring (MRM) mode of the individual compounds**

<b>Compound name</b>	<b>Parent ion (m/z)</b>	<b>Daughter ion (m/z)</b>	<b>Dwell time (S)</b>	<b>Cone (v)</b>	<b>Collision (v)</b>
<b>PFHp - C7</b>	363 (-)	319	0.05	15	15
<b>PFOA - C8</b>	413 (-)	369	0.05	15	15
<b>PFOS - C8</b>	499 (-)	99	0.05	15	40
<b>PFNA - C9</b>	463 (-)	419	0.05	15	14
<b>PFDA - C10</b>	513 (-)	469	0.05	15	15
<b>PFUnDA - C11</b>	563 (-)	523	0.05	15	15
<b>Bisphenol A</b>	227 (-)	212	0.075	32	28
<b>Acetaminophen</b>	152 (+)	110	0.075	25	15

#### **4.4 Results of Perfluorinated Compounds, Bisphenol A and Acetaminophen**

This section presents the results obtained from the analysis of the selected emerging contaminants in different treatment stages of the four selected wastewater treatment plants. The emerging contaminants selected include bisphenol A, acetaminophen and six types of perfluorinated compounds namely, perfluorooctanoic acid (PFOA), perfluorooctane sulphonate (PFOS), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA),

perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUDA) and were chosen due to their extensive use and their harmful effects on both aquatic life and humans. The method of simultaneous determination of these sets of contaminants was also validated using Ultra-performance liquid chromatography tandem mass (UPLC/MS/MS).

#### 4.4.2 Method Linearity and Sensitivity

For all the studied emerging contaminants, desirable linearity in detector response was obtained over the range of 0.1 - 1000 ng/L (for all PFCs) and 50 – 2000ng/L (for bisphenol A and acetaminophen) with correlation coefficients ( $R^2$ ) of  $\geq 0.998$  for all transitions. The retention time obtained (Table 4.2) for all the analytes (especially for acetaminophen) is among the shortest retention time reported in the literature (Thomas et al., 2007; Shivakoti, 2010; Anumol et al., 2013) for the studied emerging contaminants.

The method sensitivity is dependent on the levels of interferences present in the blank and in the solvents used. Limits of detection (LODs) and limits of quantitation (LODs) were defined as S/N ratio of 3 and 10, respectively. LOD and LOQ are shown in (Table 4.2). LODs ranged from 0.014 – 0.036  $\mu\text{g/L}$ , and LOQs ranged from 0.047 – 0.686  $\mu\text{g/L}$ .

**Table 4: Retention time, limit of detection (LOD), limit of quantification (LOQ), and correlation coefficients ( $R^2$ ) of the analytes**

<b>Compound Name</b>	<b>Retention Time (min)</b>	<b>LOD (<math>\mu\text{g/l}</math>)</b>	<b>LOQ (<math>\mu\text{g/l}</math>)</b>	<b><math>R^2</math></b>
<b>PFHpA</b>	6.73	0.025	0.08	0.998
<b>PFOS</b>	7.44	0.023	0.075	0.999
<b>PFNA</b>	8.03	0.019	0.064	0.999
<b>PFOS</b>	8.06	0.027	0.083	0.998
<b>PFDA</b>	8.52	0.021	0.686	0.999
<b>PFUnA</b>	8.92	0.036	0.114	0.998
<b>Acetaminophen</b>	1.17	0.023	0.077	0.999
<b>Bisphenol A</b>	5.87	0.014	0.047	0.999

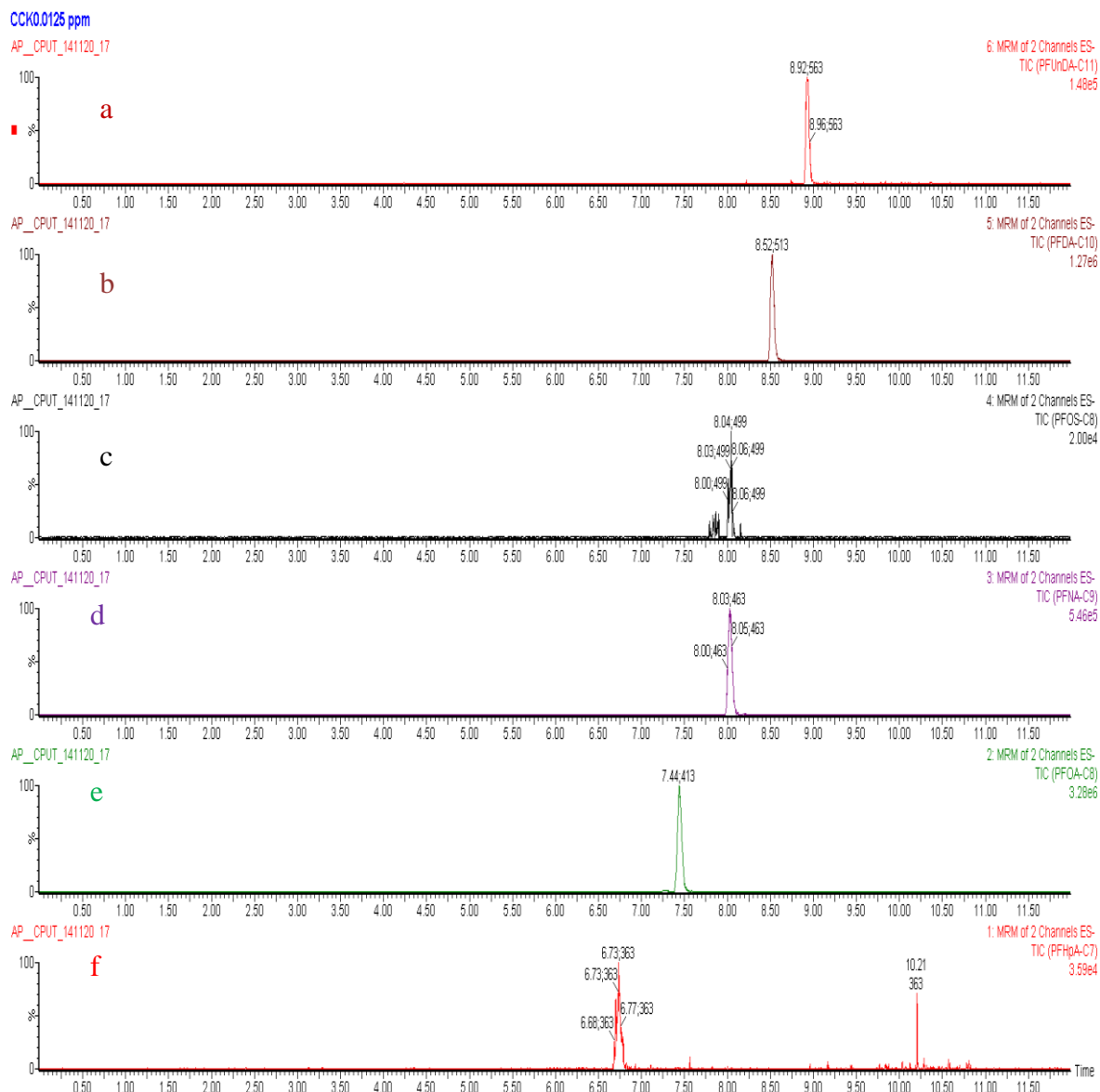


Figure 4.6: Chromatograms of (a) Perfluoroundecanoic acid (PFUnA, RT = 8.92 min), (b) Perfluorodecanoic acid (PFDA, RT = 8.52min), (c) Perfluorooctane sulfonate (PFOS, RT = 8.06 min), (d) Perfluorononanoic acid (PFNA, RT = 8.03 min), (e) Perfluorooctanoic acid (PFOA, RT = 7.44 min) (f) Perfluoroheptanoic acid (PFHpA, RT = 6.73 min) detected in negative ion mode.

## 10 ppm A&B

AP\_CPUT\_150609\_13

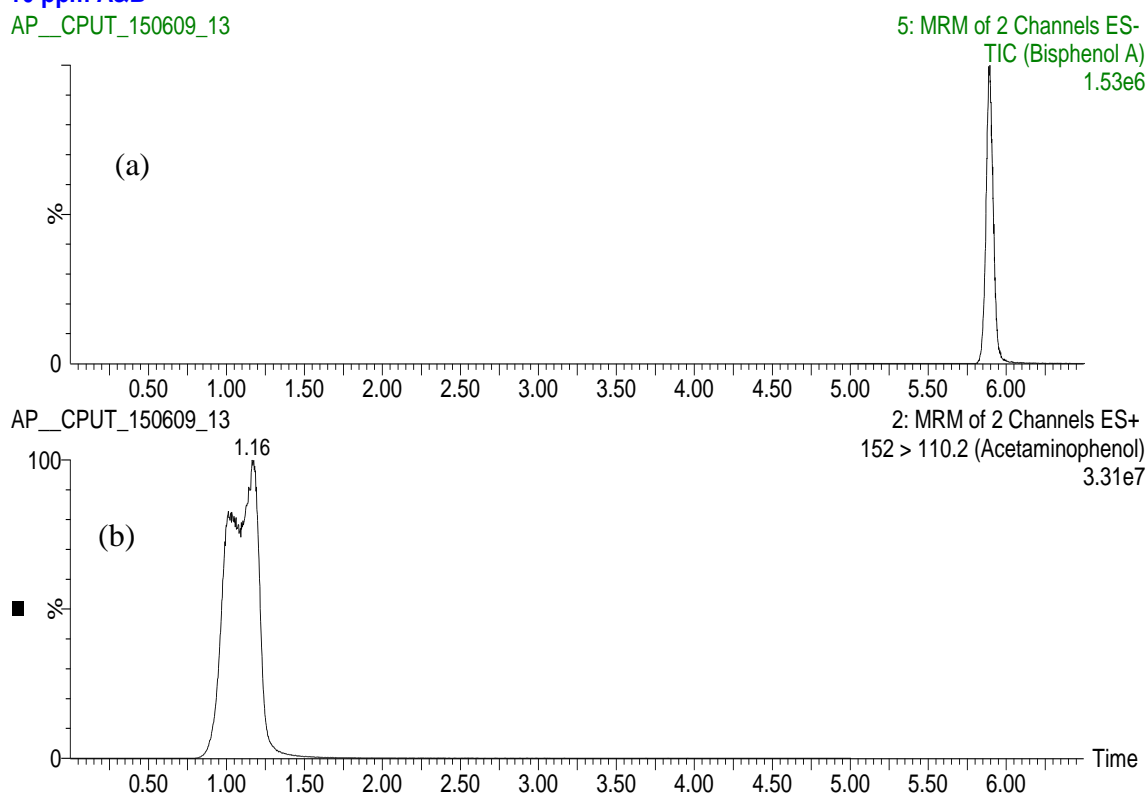


Figure 4.7: Chromatograms of (a) bisphenol A (RT = 5.87 min), (b) acetaminophen (RT = 1.16) standard solutions

Furthermore, Figures 19 and 20 shows the chromatograms obtained for the analytes at a concentration of 12.5  $\mu\text{g/L}$  for PFCs and 1000  $\mu\text{g/L}$  for bisphenol A and acetaminophen at the applied SRM transitions and the calibration curves for each analyte are shown in Appendix E - L.

### 4.4.3 Level of PFCs in Wastewater.

The average PFC concentration in the studied WWTPs is presented in Table 4.3. PFNA is the most predominant of all the six targeted PFCs, followed by PFOA and PFNA. They are detected in the influent of all the WWTP. PFOA and PFNA are also detected in all the WWTPs effluent except in Beaufort West and Scottsdale WWTPs respectively. PFCs concentrations in this study are similar to that of Arvanitia et al., (2012) and sun et al., (2011) and lower than the reported values of WWTPs effluent from some other countries. PFOS were not detected in two out of the four sampled WWTPS (Beaufort West and Zandvliet). The highest PFOS concentration (ranging from 10.24 - 9.30 ng/L) was found in Bellville WWTP, which receives inflow from both municipal, industrial and landfill leachates. PFOS was not detected in Scottsdale WWTP influent but was detected in the

plant effluent. Higher levels of PFOA, PFNA and PFOS have been found in a wastewater treatment plant in Kanto area, Japan at concentrations of 10 - 68 ng/L, 17 - 94 ng/L and 42 - 635 ng/L respectively (Murakami et al., 2009). Additionally, high PFOS concentrations range of 18 – 449 ng/L and 16 – 303 ng/L have been reported in wastewater influent and effluent respectively (Huset et al., 2008). Generally, there is a noticeable decrease in the PFC concentration from the influent to effluent. This decrease could be explained in term of sorption of the contaminants onto the activated sludge (Sun et al., 2011; Arvanitia, et al., 2012). Some exceptions were noted in the level of PFOA and PFHpA in - between the treatment process.

There were observed increase in the concentration of PFHpA and PFOA (in Beaufort West WWTP) after activated sludge treatment. Additionally, PFOA and PFOS have been identified to be non-biodegradable by activated sludge process (Sinclair & Kannan, 2006). There was also an increase in their concentrations in the effluent of Zandvliet, Bellville and Scottsdene WWTPs. A similar phenomenon was also reported in a study by Sinclair and Kannan (2006), Loganathan et al., (2007) and Chularueangaksorn et al., (2012). Chularueangaksorn et al., (2012) attributed the increase in PFC concentration in the treatment plant and effluent to subsequent release of the adsorbed contaminants from the sludge into the new inflow. It was also suggested that degradation of some PFC precursors such as sulphonamides and fluorotelomer alcohols through treatment process could form additional sources of PFOA and PFOS in the treatment plants.

Since PFCs are emerging contaminants, presently there are no available guidelines limits for these contaminants in wastewater effluent. In a few countries, there are guideline values for some PFCs in drinking water. As discussed in chapter 2 (section 2.3.7), the guideline values for PFOS and PFOA in drinking water according to the USEPA are 200 and 400 ng/L respectively. In Germany, a precautional limit of 500 ng/L was set as the tolerable level for PFOA and PFOS in drinking water, tolerable for one year of consumption. PFOA health risk of 300 ng/L and 40 ng/L are limits for Minnesota and New Jersey respectively. Relating the result of PFCs found in Beaufort West WWTP which is a drinking water source to the available guidelines in literature, it can be concluded that the level in the effluent is low and might not have any toxic effect on human. Furthermore, there is no general limit value and no proven evidence yet for PFCs toxicity at the specified concentration.

#### **4.4.4 Comparison of Removal of PFCs in the Wastewater Treatment Plants**

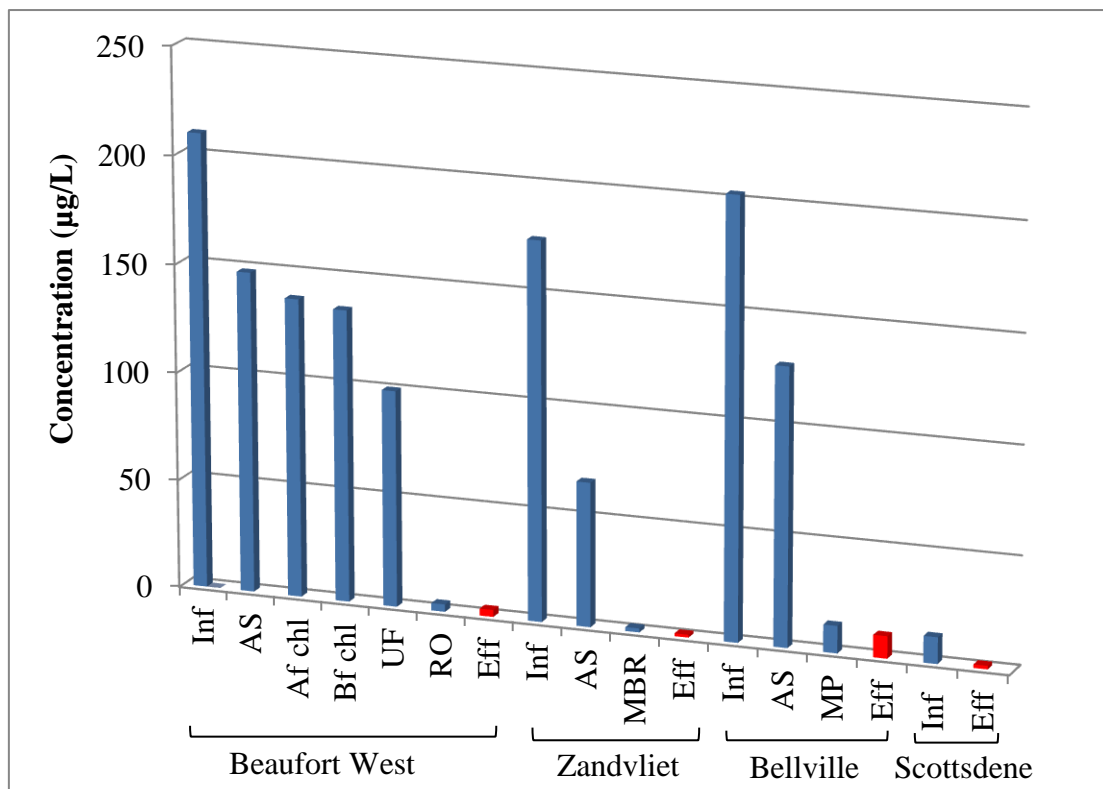
The removal efficiencies for total PFCs in the studied WWTPs ranged from 52.1 to 96.4% (Table 4.3). Of all the studied PFCs, PFHpA (a perfluorocarboxylic acid with the shortest carbon chain in this study) shows the highest removal efficiency. This can be attributed to the chain length and high water solubility nature. The highest percentage of total PFCs removal was found in Beaufort West WWTP (96.4%), followed by Zandvliet (65%), Scottsdene WWTP (54%) and Bellville (52%). This study indicates that, the available treatment process in Beaufort West WWTP was able to effectively remove > 96.4% of targeted PFCs in the wastewater and partially removed ( $\leq 65\%$ ) in the other three plants. The application of tertiary treatment process and the advanced oxidation process in Beaufort West WWTP helps in high removal of the contaminants. Although an increase in the concentration of PFNA and PFDA was observed after ultrafiltration, there was high removal after reverse osmosis and UV/H<sub>2</sub>O<sub>2</sub>. The level of PFCs found in the WWTPs effluent provides evidence that these contaminants are regularly released into receiving waters. Also, the advanced treatment process in Beaufort West plant had shown that there are still some traces of PFCs in Beaufort West reclaimed water which is used for drinking and household purposes. PFCs have been identified in drinking water in the Western Cape. High PFHpA values ranged from ND – 37.48 ng/L and ND – 43.8 ng/L has been detected in drinking water plant influent and effluent respectively (Booi, 2013).

**Table 5: Summary of the result of perfluorinated compounds in all WWTPs. Values in parentheses are the relative standard deviations (RSDs; n = 3). Detectable responses below the LOD were reported as non – detected (ND)**

	Treatment	PFHPA	PFOA	PFNA	PFOS	PFDA	PFUnDA	∑PFCs
		<b>(ng/l)</b>						
<b>Beaufort West</b>	Influent	35.14 ± 0.06	3.23 ± 0.69	18.8 ± 0.13	ND	6.21 ± 0.28	2.66 ± 0.41	66.04
	Activated sludge	22.10 ± 0.22	ND	13.43 ± 0.74	ND	5.88 ± 0.12	2.32 ± 0.06	
	Before chlorination	22.23±0.33	4.95 ± 0.07	12.11 ± 0.02	ND	1.01 ± 0.05	2.32 ± 0.48	
	After chlorination	21.92 ± 0.26	5.25 ± 0.02	11.09 ± 0.10	ND	1.08 ± 0.03	2.44 ± 0.08	
	After ultrafiltration	ND	ND	18.73 ± 0.25	ND	2.04 ± 0.08	1.64 ± 0.12	
	After reverse osmosis	20.12 ± 0.04	ND	7.52 ± 0.10	ND	ND	1.42 ± 0.12	
	After UV/H <sub>2</sub> O <sub>2</sub>	ND	ND	1.12 ± 0.05	ND	ND	1.23 ± 0.09	2.35
<b>% Removal</b>								<b>96.4%</b>
<b>Zandvliet</b>	Influent	48.53 ± 0.20	7.32 ± 0.28	10.20 ± 0.08	ND	ND	ND	66.05
	CAS	32.32 ± 0.06	7.53 ± 0.04	10.10 ± 0.23	ND	ND	ND	
	MBR	ND	5.62 ± 0.07	10.50 ± 0.06	ND	ND	ND	
	Effluent	ND	13.10 ± 0.27	10.03 ± 0.12	ND	ND	ND	23.13
<b>% Removal</b>								<b>64.9%</b>
<b>Bellville</b>	Influent	22.78 ± 0.21	2.59 ± 0.14	32.30 ± 0.62	9.50 ± 0.17	3.25 ± 0.59	3.23 ± 0.07	73.65
	After aneorobic	9.21 ± 0.04	2.32 ± 0.03	19.84 ± 0.08	9.30 ± 0.04	1.87 ± 0.04	2.67 ± 0.02	
	Maturation pond	8.21 ± 0.69	7.34 ± 0.49	15.52 ± 0.29	10.20 ± 0.27	ND	1.03 ± 0.21	
	Effluent	7.62 ± 0.26	7.22 ± 0.115	10.20 ± 0.22	10.24 ± 0.06	ND	ND	35.28
<b>% Removal</b>								<b>52.1%</b>
<b>Scottsdene</b>	Influent	6.10 ± 0.22	3.17 ± 0.24	ND	ND	ND	4.22 ± 0.24	13.49
	Effluent	ND	4.01 ± 0.08	ND	1.02 ± 0.01	ND	1.13 ± 0.05	6.16
<b>% Removal</b>								<b>54.3%</b>

#### 4.4.5 Level of BPA and Wastewater Treatment Plants Performance

The average level of bisphenol A in the studied WWTPs is presented in Figure 4.8 and Appendix D. Bisphenol A was detected in all the treatment stages of the four WWTPs. The level in the influents of the four WWTPs ranged from 12 - 210 µg/L and the effluents concentrations ranged from 1.3 – 10.3 µg/L. As expected, the levels of BPA were higher in the influents compared to effluents as there were no precipitations in days prior to samplings. The highest BPA level in the influent was found in the Beaufort West WWTP, followed by Bellville WWTP at concentrations of 210.1 and 203.1 µg/L respectively.



**Figure 4.8: Concentration levels of bisphenol A in wastewater at different stages of treatment.** Inf=influent, AS=activated sludge, Bf chl= before chlorination, Af chl=after chlorination (reclamation plant inflow), UF=ultra-filtration, RO=reverse osmosis, MBR=membrane bioreactor, MP=maturation pond, and Eff=effluent.

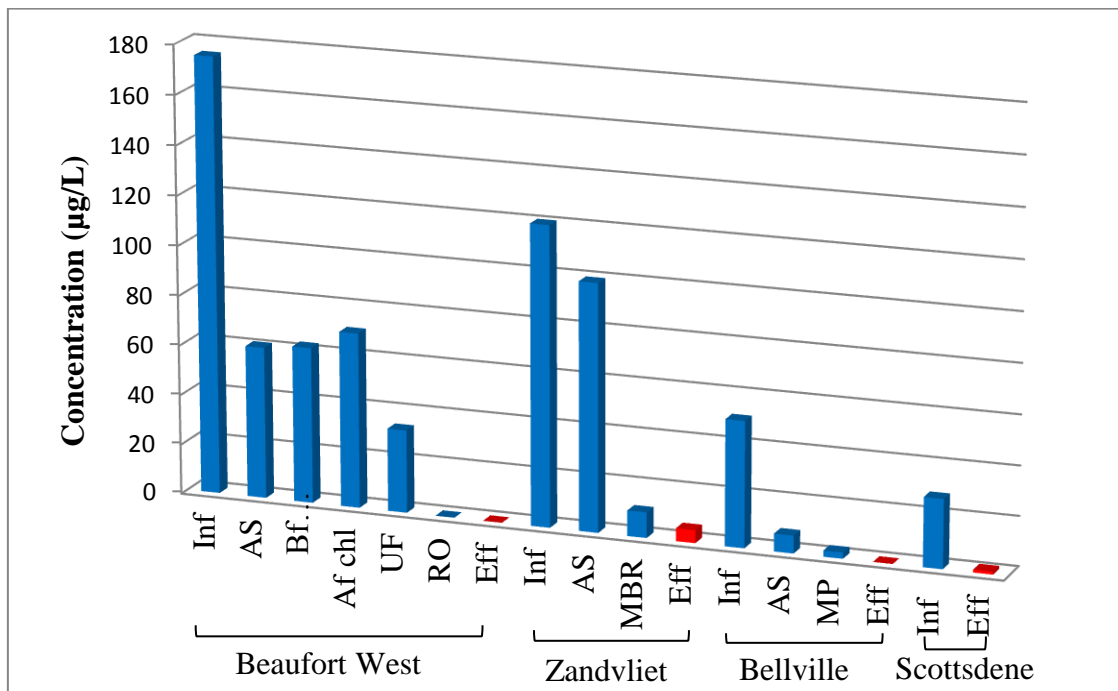
Influent BPA level in this study was extremely high compare to the values reported by other authors (Mohapatra, et al., 2011). This suggests significant sources of BPA in the waters entering the WWTPs. Based on the properties of BPA, such as its low vapour pressure and moderate solubility in water, washing residue produced in the manufacture and handling of application materials (such as polycarbonates and epoxy resins) and wastewater from

industries have been identified as the most common industrial sources of BPA in the environment (Mohapatra et al., 2011). Also, as previously discussed recycling paper products like toilet paper is considered as a significant source of BPA in municipal wastewater. The concentrations of BPA in this study (especially in Beaufort West and Bellville WWTPs) are closely related to values reported by Olujimi et al., (2013) in Cape flat WWTP, Cape Town, South Africa. From the results (see Figure 4.8), it can be noted that the BPA concentration of the effluent is proportional to the influent. Although these WWTPs are not specifically designed to eliminate BPA from wastewater, a major decrease through the different treatment processes was observed. In this study, conventional activated sludge and membrane bioreactors effectively removed BPA. Reduction from influent through the effluents was observed in all the treatment plants. High reduction in the concentration of BPA after activated sludge treatment stages were observed in Beaufort West, Zandvliet and Bellville WWTP. Similar BPA removal rates (> 90%) was reported in a study by Clara et al., (2005) in both membrane bioreactors and conventional WWTP. The high removal could be related to the biodegradation and/or adsorption of the compound upon dissolved solids during this stage in the system. The overall BPA removal efficiencies of Beaufort west, Zandvliet, Bellville and Scottsdale WWTPs were 98.5%, 99.7%, 93.4%, and 86.5% respectively. In view of the low effluent concentrations, biodegradation/biotransformation processes are considered the main removal pathway for BPA. Better removals were observed with MBR compared with CAS (as shown in Figure 4.8). The low vapour pressure ( $8 \times 10^{-10}$  –  $4 \times 10^{-7}$  mm Hg) of BPA show its poor volatilization during the treatment process, consequently confirming the fact that the different treatment stages applied in the WWTPs were effective in removing the contaminants from wastewater.

Thus, the treatment processes applied in the four treatment plants seem effective for BPA removal from influent to effluent. Even though all the studied WWTPs applied different treatment processes, they do have comparable activated sludge as solid waste in the secondary treatment stage. Studies have shown that activated sludge is very efficient in estrogenic compounds removal from wastewater treatment plants, but the compounds may leach from the solids at a later stage as complete lifecycle have not been established.

#### 4.4.6 Level of Acetaminophen and Wastewater Plants Treatment Performance.

The average level of acetaminophen in each studied WWTPs is presented in Figure 4.9 and Appendix D. The concentration ranged from 27.98 - 175.11  $\mu\text{g/L}$  and ND – 5.23  $\mu\text{g/L}$  in the influents and effluents respectively. The high concentration in wastewater influent is expected since acetaminophen is an over the counter drug and can be purchased without prescription.



**Figure 4.9: Concentration levels of acetaminophen in wastewater at different stages of treatment.** Inf=influent, AS=activated sludge, Bf chl=before chlorination, Af chl=After chlorination (reclamation plant inflow), UF=ultra-filtration, RO=reverse osmosis, MBR=membrane bioreactor, MP=maturation pond, and Eff=effluent.

Compared to the other studied WWTPs, highest influent acetaminophen concentration was observed in Beaufort West and the concentrations were up to three fold higher when compared to results of wastewater influent obtained by Agunbiade and co-workers, (2014). Although the population equivalent and the average mass flow (see Table 3.1) of the plant (Beaufort West) is lower than that of Zandvliet and Bellville WWTPs. This indicates that the influent concentrations depend chiefly on the degree of the drug prescription, as well as human metabolism, which suggests high consumption of the drug in the area or accumulation in water during repeated cycling of the same water during reuse. In all the WWTPs, there was observable reduction in acetaminophen concentration of the effluents compared to the influents. In Beaufort West WWTP, there was an observed increase in the

level of acetaminophen after chlorination. Although there is no literature that confirm the increase in the level of acetaminophen with chlorine disinfection, studies have shown that acetaminophen is transformed by chlorination to produce toxicants such as N-acetyl-p-benzoquinone imine and 1,4-benzoquinone (Bedner & MacCrehan, 2006; Hrudey & Charrois, 2012). With this fact, it can be concluded that the increase in the acetaminophen level can be due to unidentified sources in the treatment plant, suspected to be from a previously accumulated spike in the settling tank. In Zandvliet WWTP, it was observed that the activated sludge system applied in this plant removed less acetaminophen compared to Beaufort West and Bellville WWTPs. Additionally, there was an observed better removal of acetaminophen with the membrane bioreactor compared to the convectional activated sludge treatment process. This was also observed in a study by Ranjenovic et al., (2007), who reported 99.8% and 98.4% acetaminophen removal efficiency in wastewater was reported for membrane bioreactor and convention activated sludge processes respectively. Higher removal of bisphenol A by a membrane bioreactor compared to conventional activated sludge was also observed in this study (Figure 4.9). The better removal efficiency of readily biodegradable micropollutants by membrane bioreactor could be associated with the smaller flock size of the medium, which improves mass transfer by diffusion and consequently leads to an increased elimination (Radjenovic et al., 2007).

#### **4.5 SUMMARY OF CHAPTER**

The main objective of this chapter was to identify and quantify PFCs, bisphenol A and acetaminophen in wastewater treatment plants, and to check the water quality parameters for these compounds by analysing the influents and effluents of plants in the Western Cape. The aim was to evaluate the performance of treatment methods on the removal of the organic pollutants. Also, to determine the effluent quality in terms of the water quality parameters; to assess if these parameters are within the South African and WHO guideline for effluent discharge and drinking water quality for Beaufort West treatment plant which is a drinking water source. The result obtained shows that the analysed contaminants were present in the influents to the four wastewater treatment plants of the Western Cape. Higher levels of bisphenol A and acetaminophen were identified in the treatment plants influent, compared to the level of PFCs. This confirmed the high use of bisphenol A in the manufacturing of household essentials and the read availability of acetaminophen without prescription. It was observed that plants with tertiary and advanced oxidation treatment processes removed the contaminants better but transformation by-products were not tested for, thus the emerging contaminants removal is not conclusive. The results also confirmed that acetaminophen is

easily removed in treatment plants as there were an observed reduction in the concentrations from influent to effluent in all the treatment plants. Conversely, the final effluent of some treatment plants had higher level of PFC compared to the plants influent. This might be due to the degradation of PFC precursors or some other possible source of contaminations within the treatment plants. Lastly, the level of water quality parameters (pH, temp, TDS, EC, P COD and TOC) in the final effluents of all the treatment plants are within the South African guideline and the World Health Organization limit recommended for effluent discharge, while the nitrite/nitrate levels of all the wastewater treatment plant effluents exceeded the maximum allowable limit set SA and WHO for effluent discharge.

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 Introduction

This section of the thesis presents the conclusion, recommendations and areas that requires further studies.

#### 5.2 CONCLUSION

Globally, ground water and (most importantly) surface water (rivers and dams) are the major sources of water. Unfortunately, the qualities of this resource are being threatened by the increasing amount of contaminants being released by human activities. Thus, with the use of treated wastewater as alternative source of potable water which is now gaining more recognition and approval, strict treatment measures must be put in place to ensure the delivery of clean and toxin-free water to the communities. In South Africa, the demands on water for household, industrial, commercial, as well as, agricultural purposes are critically increasing, while the national available freshwater supplies are decreasing. Compounding this problem is the unceasing contamination of surface water sources via indiscriminate discharge of sewage or poorly treated wastewater. There is a growing concern about the presence of emerging contaminants in wastewater effluents for reuse or discharge into our environment due to their potential negative effects on the human population and aquatic species. Hence, it is imperative to monitor the efficiencies of the available wastewater treatment technologies by developing standardized analytical methods that can effectively identify and quantify these contaminants and all their degradation by-products so that proper regulation and control can be put in place.

In this study, a simple, precise, fast and accurate analytical method was developed for the simultaneous determination of perfluorooctanoic acid, perfluoroheptanoic acid, perfluorononanoic acid, perfluorooctane sulfonate, perfluorodecanoic acid, perfluoroundecanoic acid, bisphenol A and acetaminophen in water. Solid phase extraction cartridges used for the simultaneous extraction of target contaminants in wastewater were optimized and Oasis hydrophilic - lipophilic balanced (HBL) cartridges gave a better recovery than the Strata X cartridges. The analytical instrument (UPLC/MS/MS) used identified the presence of the target contaminants in the standards as well as the real samples and their characteristic ions were confirmed. The developed method in this study was

applicable to real wastewater samples. Furthermore, the idea of drying the final extract under a gentle stream of nitrogen and reconstituting it to 2 mL gave an accurate account of the actual volume of the final extract used for the instrument analysis.

The study successfully identified and quantified the selected emerging contaminants in the wastewater samples from four WWTPs in Cape Town and environs, namely; Beaufort West, Zandvliet, Bellville and Scottsdale WWTPs. The results obtained were appropriate for the evaluation of the treatment capacity of the wastewater treatment techniques for the removal of the target analytes. Almost all (up to 90%) of the targeted contaminants were found in the influent of the treatment plants in relatively high concentrations. Perfluorooctane sulfonate was not detected in the influents of Beaufort West, Zandvliet and Scottsdale WWTPs. Both perfluorodecanoic acid and perfluoroundecanoic acid were not detected in Zandvliet WWTP influents. The concentration of bisphenol A and acetaminophen was high in the influent and relatively low in the effluent. The percentage removal of bisphenol A and acetaminophen include 98.5% and 100% in Beaufort West, 99.7% and 95.6% in Zandvliet, 93.4% and 100% in Bellville and 86.5% and 95.8% in Scottsdale WWTP respectively. This reflects that the contaminants were well removed by the treatment process in all the four treatment plants. The concentrations and the removal efficiencies of total perfluorinated compounds were much lower than bisphenol A and acetaminophen. The percentage removal of total PFCs in Beaufort West, Zandvliet, Bellville and Scottsdale WWTPs are 96.4%, 64.9%, 52.1% and 54.33% respectively. To some extent, the conventional sewage treatment processes were relatively efficient to remove these compounds from wastewaters. Although, a certain amount of the compounds still escaped the treatment and are released into the environment. This further confirms that the existing conventional WWTPs are not designed for effective degradation of the targeted contaminants. Advanced treatment processes applied in Beaufort West and Zandvliet shows a significant removal efficiency of the targeted contaminants. Bellville and Scottsdale WWTPs show poor removal (less than 55%) of PFCs even though the influent concentrations of these plants were lower than that of Beaufort West and Zandvliet WWTPs contaminants. High percentages removal of targeted contaminants observed for the treatment plants may still not be sufficient to offer protection to the aquatic environment as the remaining percentage in the effluent may be sufficient to pose negative impacts and many breakdown pathways result in transformation by-products that are more toxic than the parent compounds. In addition, the 100% acetaminophen removal observed in some treatment plants does not completely imply elimination of the toxic metabolites, transformation compounds and other chemicals in the treatment plant

effluents as the conventional process moves the contaminants from liquid to solid phase and the solid phase need testing and careful disposal. Furthermore, it is difficult to relate the results of the level of the organic contaminants found in this study to the effluent discharge quality and to the effects on aquatic organisms and human because there have not yet been global implemented guidelines for these compounds and their metabolites in wastewater discharge.

The study of physicochemical parameters of the wastewater shows that not all the studied pollutants were reduced in the wastewater after the treatment processes, which indicates sources of contamination or high variability within the treatment plants. The level of pH, temperature, electrical a conductivity, total dissolved solids, carbon oxygen demand, total oxygen demand and orthophosphate in the final effluents of all the wastewater treatment plants are within the South African and World Health Organisation guideline limits. The TOD and COD values were reduced in all the treatment plants (except Zandvliet WWTP) to a large extent which indicates the removal of organic content. However, a very high level of nitrate/nitrite, which is non-compliant with acceptable limits, was observed in the effluent of all the treatment plants. The high nutrient level of the effluent could cause eutrophication of the receiving water bodies and could cause other severe pollution problems. The impact of polluted water on the environment and human health as well as the economy can be disastrous. Poor water quality can result in increased costs of treatment of drinking and industrial process water, as well as a decrease in agricultural yields. In conclusion, regulatory and constant monitoring programs should be implemented and encouraged in South Africa, in order to ensure good treatment practice and proper quality wastewater discharge into the environment and complete for domestic reuse. It is clear from this study that uniformity in treatment efficiency is not achieved at different WWTPs.

### **5.3 RECOMMENDATIONS**

This study reported the detection and quantification of perfluorinated compounds, bisphenol A and acetaminophen in wastewater treatment plants. From the results, it was observed that higher effluent concentrations were measured for some PFCs, which could be related to the compound precursors that may be transformed into the studied compounds during treatment. Therefore, it is essential to analysis for PFCs precursors and secondary breakdown products in the wastewater treatment plant in order to have a broader understanding of their degradation phenomena. Studies should be done to check the effect of the effluents on the

physicochemical quality of the receiving watershed and the relative bioaccumulation of these compounds in the aquatic environment on exposed species.

To ensure improvement in treatment and compliance of wastewater treatment with future discharge requirements in South Africa, particularly with regards to the emerging contaminants, it is recommended that the existing wastewater treatment plants are upgraded and new advanced treatment technologies are implemented and no raw sewerage is discharged.

#### **5.4 AREAS OF FURTHER STUDIES**

There is limited or no information on the behaviour of emerging contaminants in the receiving water in South Africa, thus, further studies are recommended on the occurrence, fate, and effects of these substances in the environment and on humans.

The World Health Organization and the South Africa Bureau of Standards should look also into establishing guideline limits for these contaminants.

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## APPENDIX

### Appendix A: Raw data obtained from the validation of solid Phase extraction Cartridge using Oasis HLB

#### DATA OF OASIS

Analytes	In ultrapure water at 10 µg/L			In Wastewater at 10 µg/L			
	Measured (µg/L)	conc.	%RSD	Average % Recoveries	Measured conc. (µg/L)	%RSD	Average % Recoveries
PFHpA	9.47 ± 0.329		3.47	94.7	9.03 ± 0.39	4.32	90.0
PFOA	10.2 ± 0.425		4.12	102	9.84 ± 0.63	6.4	98.3
PFNA	10.0 ± 0.714		7.12	100	10.0 ± 0.82	8.19	100
PFOS	9.80 ± 0.708		7.23	98	9.52 ± 0.16	1.67	95.0
PFDA	9.86 ± 0.557		5.65	98.6	9.99 ± 0.05	0.53	99.0
PFUNDA	8.75 ± 0.671		7.67	87.5	9.05 ± 0.04	0.45	90.5
Acetaminophen	8.25 ± 0.478		5.79	82.5	7.93 ± 0.13	1.68	79.3
Bisphenol A	9.92 ± 0.379		3.82	99.2	10.1 ± 0.24	2.41	101.1

**Appendix B: Raw data obtained from the validation of solid Phase extraction using Stata X cartridges**

DATA OF STATA X						
Analytes	Ultrapure water at 10 µg/L			Wastewater at 10 µg/L		
	Measured conc. (µg/L)	%R SD	Average %Recoveries	Measured conc. (µg/L)	%RSD	Average % Recoveries
<b>PFHpA</b>	7.84 ± 0.354	4.32	78.4	7.54 ± 0.157	2.08	75.4
<b>PFOA</b>	10.63 ± 0.61	6.42	100.6	9.64 ± 0.195	2.02	96.4
<b>PFNA</b>	9.49 ± 0.159	8.19	94.9	9.20 ± 0.091	0.99	92.0
<b>PFOS</b>	7.54 ± 0.103	1.67	75.4	7.13 ± 0.136	1.9	71.3
<b>PFDA</b>	7.55 ± 0.183	2.42	75.5	7.13 ± 0.164	2.29	71.3
<b>PFUNDA</b>	9.56 ± 0.114	0.45	95.6	9.66 ± 0.104	1.07	96.6
<b>Acetaminophen</b>	5.72 ± 0.117	1.68	57.2	5.55 ± 0.083	1.49	55.5
<b>Bisphenol A</b>	9.73 ± 0.061	2.41	97.3	9.79 ± 0.105	1.08	97.9

## Appendix C: Raw data for water quality parameters of the four wastewater treatment plants water samples

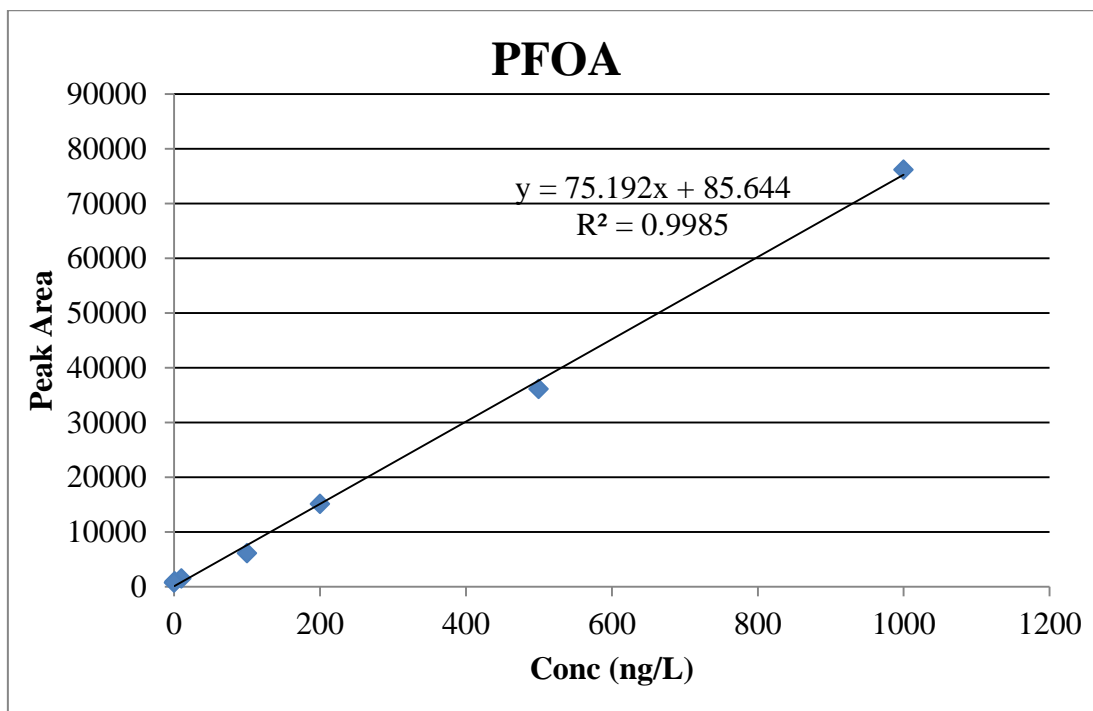
Parameters	Beaufort West WWTP		Zandvliet WWTP		Bellville WWTP		Scottsdale WWTP	
	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
<b>pH</b>	7.03 ±0.06	7.24 ± 0.04	6.89 ± 0.14	7.09 ± 0.02	6.84 ± 0.11	7.23 ± 0.08	7.35 ± 0.02	7.11 ± 0.09
<b>Electrical Conductivity (µS/cm)</b>	2271 ± 12.50	388 ± 2.88	631 ± 4.58	779 ± 5.00	1188 ± 3.21	727 ±3.51	809 ± 11.93	423 ± 3.00
<b>Total dissolve solid (mg/l)</b>	1137 ± 4.58	193 ± 4.58	315 ± 4.51	392 ± 2.52	596 ± 3.06	363 ±2.00	404 ± 2.65	211 ± 0.58
<b>Temperature (°C)</b>	19.70 ± 0.31	21.10 ± 0.35	21.0 ± 0.25	20.30 ± 0.12	19.80 ± 0.20	21.50 ±0.12	20.22 ± 0.05	19.38 ± 0.02
<b>Nitrate/Nitrite as N (mg/L)</b>	137 ± n.a.	87 ± n.a.	319 ± n.a.	249 ± n.a.	360 ± n.a.	131 ± n.a.	859 ± n.a.	428 ± na
<b>Ortho Phosphate as P (mg/L)</b>	6.7 ± na	0.05 ± na	4.9 ± na	1.3 ± na	3.7 ± na	4.3 ± na	18 ± na	1.8 ± na
<b>Total Organic Carbon (mg/L)</b>	87 ± na	1.6 ± na	126 ± na	188 ± na	136 ± na	12 ± na	44 ± na	9 ± na
<b>Chemical Oxygen Demand (mg/L)</b>	328 ± na	5.0 ± na	454 ± na	728 ± na	436 ± na	28 ± na	124 ± na	11 ± na

**Appendix D: Raw data of the level of bisphenol A and acetaminophen in wastewater samples**

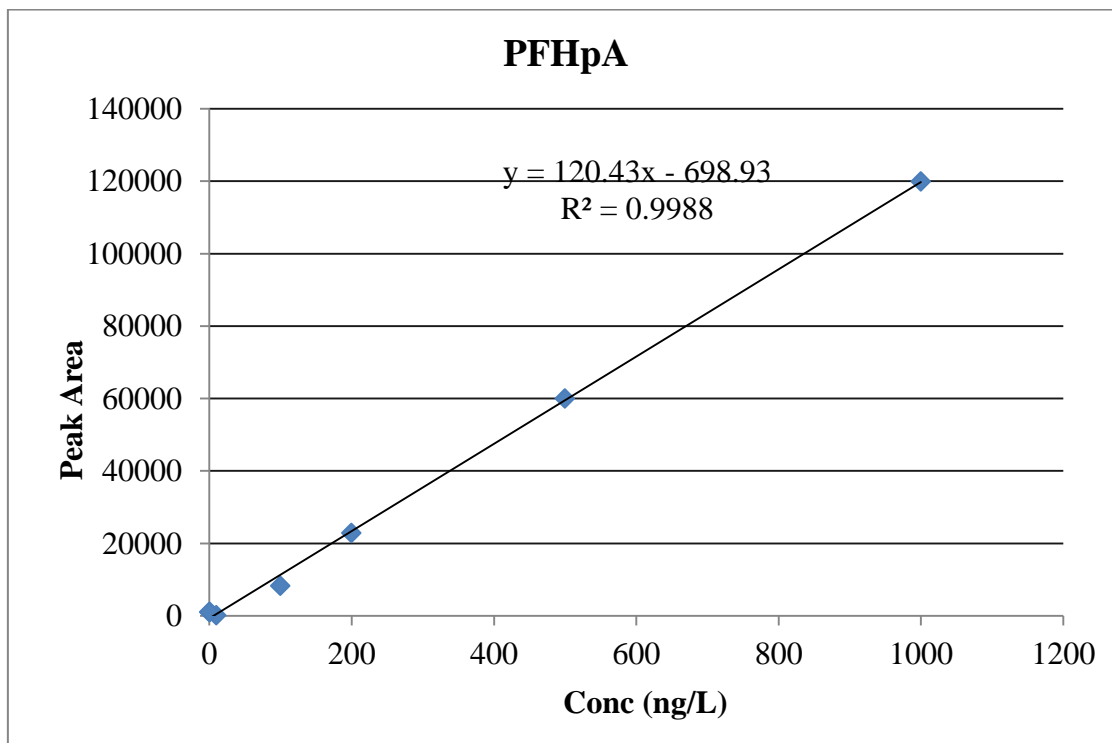
<b>Plant Name</b>	<b>Treatment Methods</b>	<b>Bisphenol A</b> ( $\mu\text{g/L}$ )	<b>Acetaminophen</b>
<b>Beaufort West</b>	Influent	210.14 $\pm 6.52$	175.11 $\pm$ 2.01
	Activated sludge treatment	148.22 $\pm 1.63$	60.93 $\pm$ 2.98
	Before Chlorination	138 $\pm 1.65$	62.64 $\pm$ 2.78
	After chlorination	135 $\pm 0.59$	70.34 $\pm$ 0.4
	Ultrafiltration	100 $\pm 1.53$	33.42 $\pm$ 1.1
	Reverse osmosis	3.43 $\pm 0.07$	ND
	After UV/H <sub>2</sub> O <sub>2</sub> (Effluent)	3.21 $\pm 0.83$	ND
<b>%Removal</b>		<b>98.5%</b>	<b>100%</b>
<b>Zandvliet</b>	Influent	173.89 $\pm 2.94$	120.32 $\pm$ 1.74
	CAS	66.81 $\pm 0.36$	99.42 $\pm$ 1.94
	MBR	1.82 $\pm 0.23$	10.33 $\pm$ 0.66
	Effluent	1.324 $\pm 0.19$	5.23 $\pm$ 0.32
<b>%Removal</b>		<b>99.7%</b>	<b>95.6%</b>
<b>Bellville</b>	Influent	203.16 $\pm 1.62$	50.86 $\pm$ 0.23
	After aneorobic treatment	128.34 $\pm 2.73$	7.19 $\pm$ 0.06
	Maturation pond effluent	12.66 $\pm 0.81$	2.43 $\pm$ 0.54
	Effluent (after chlorination)	10.34 $\pm 1.13$	ND
<b>% Removal</b>		<b>93.4%</b>	<b>100%</b>
<b>Scottsdene</b>	Influent	12.27 $\pm 1.13$	27.96 $\pm$ 0.09
	Effluent	1.66 $\pm 0.37$	1.17 $\pm$ 0.12
<b>% Removal</b>		<b>86.50%</b>	<b>95.80%</b>

After chlorination= Reclamation plant inflow, ND=Not Detected

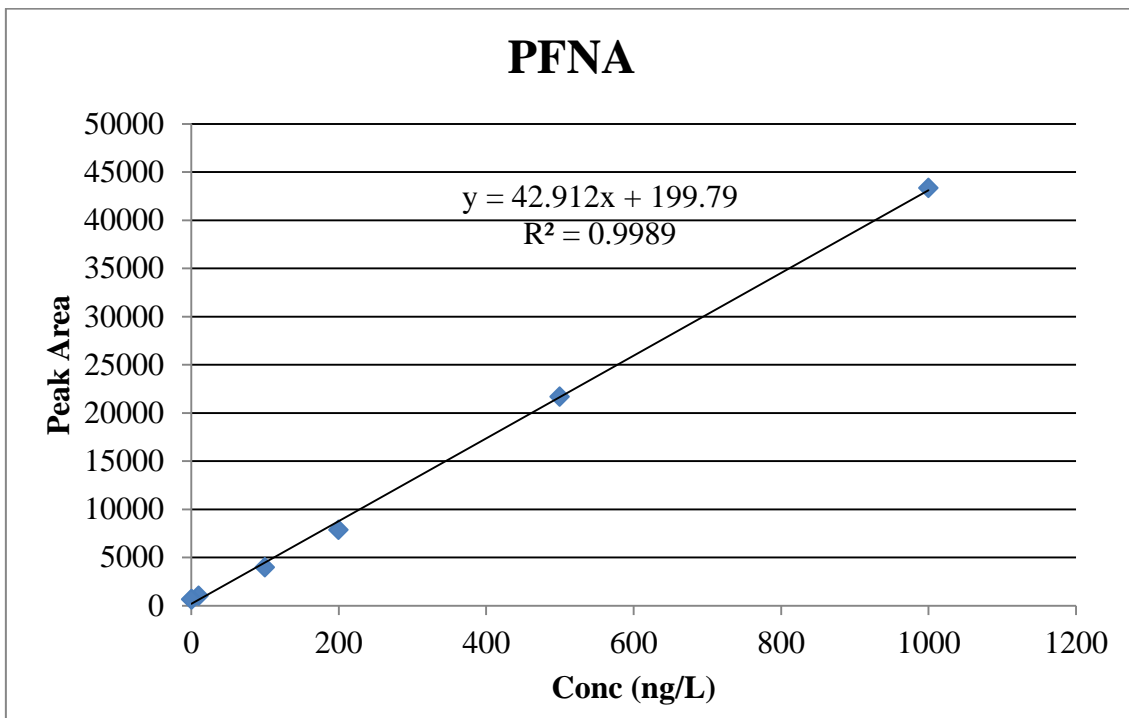
**Appendix E: Linear standard curve for perfluorooctanoic acid (PFOA)**



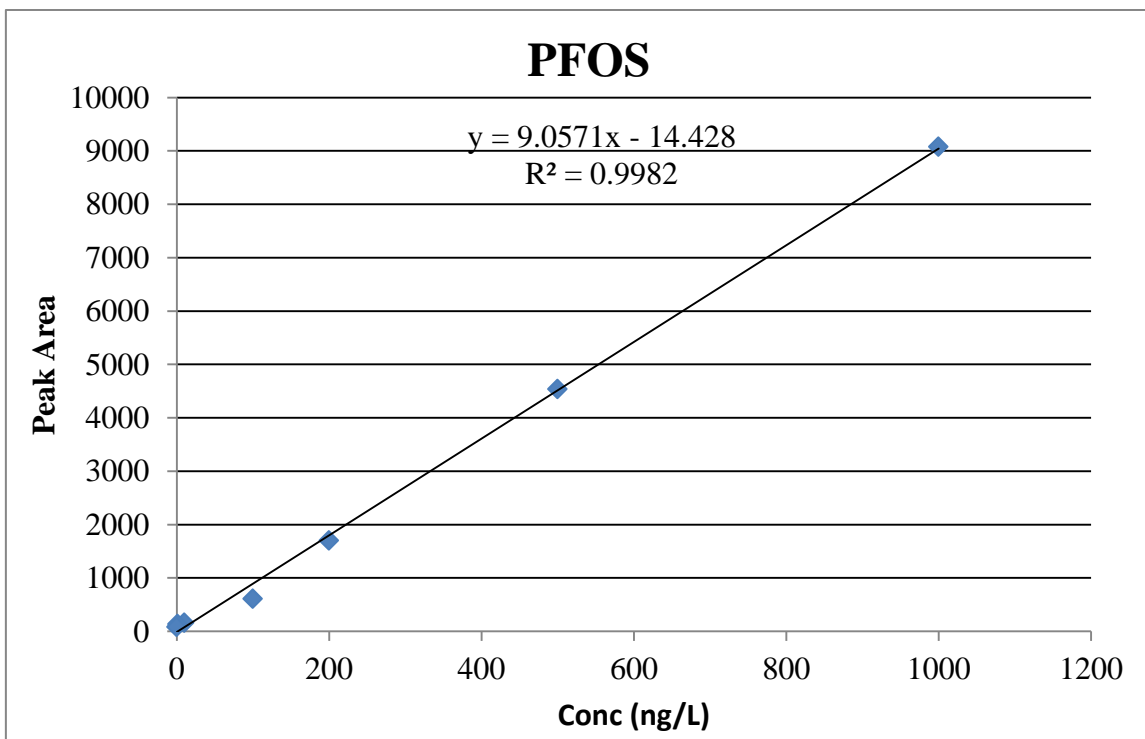
**Appendix F: Linear standard curve for perfluoroheptanoic acid (PFHpA)**



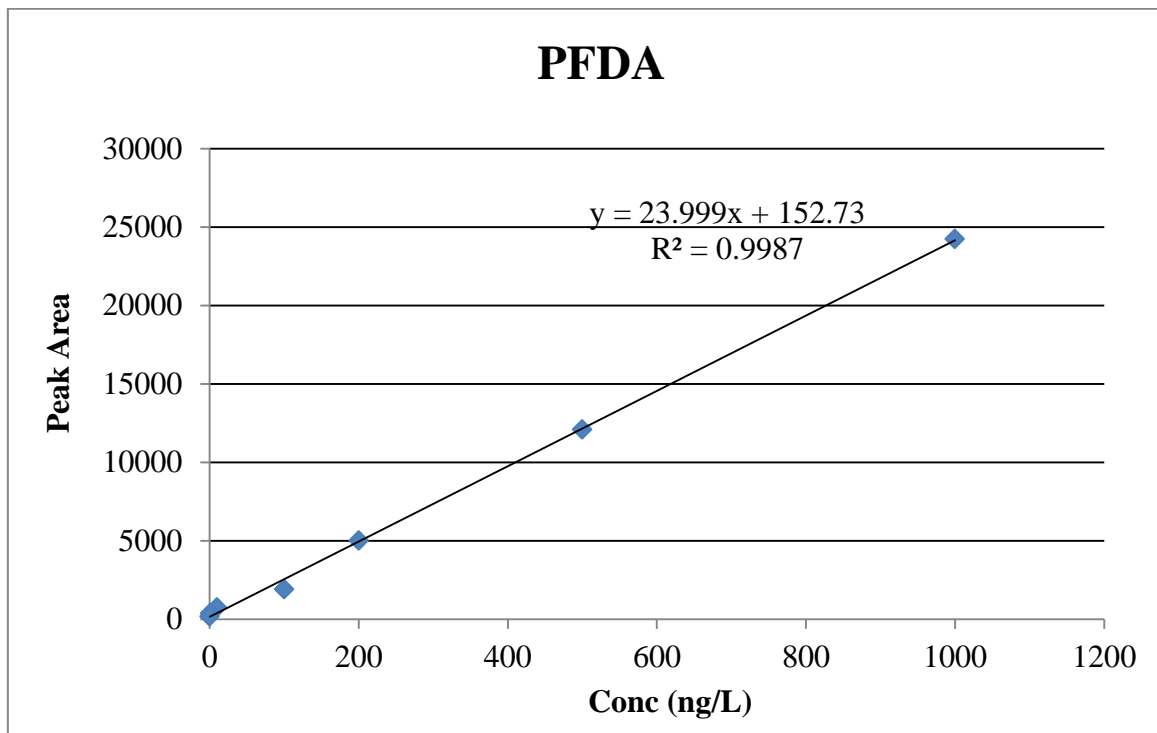
**Appendix G: Linear standard curve for perfluorononanoic acid (PFNA)**



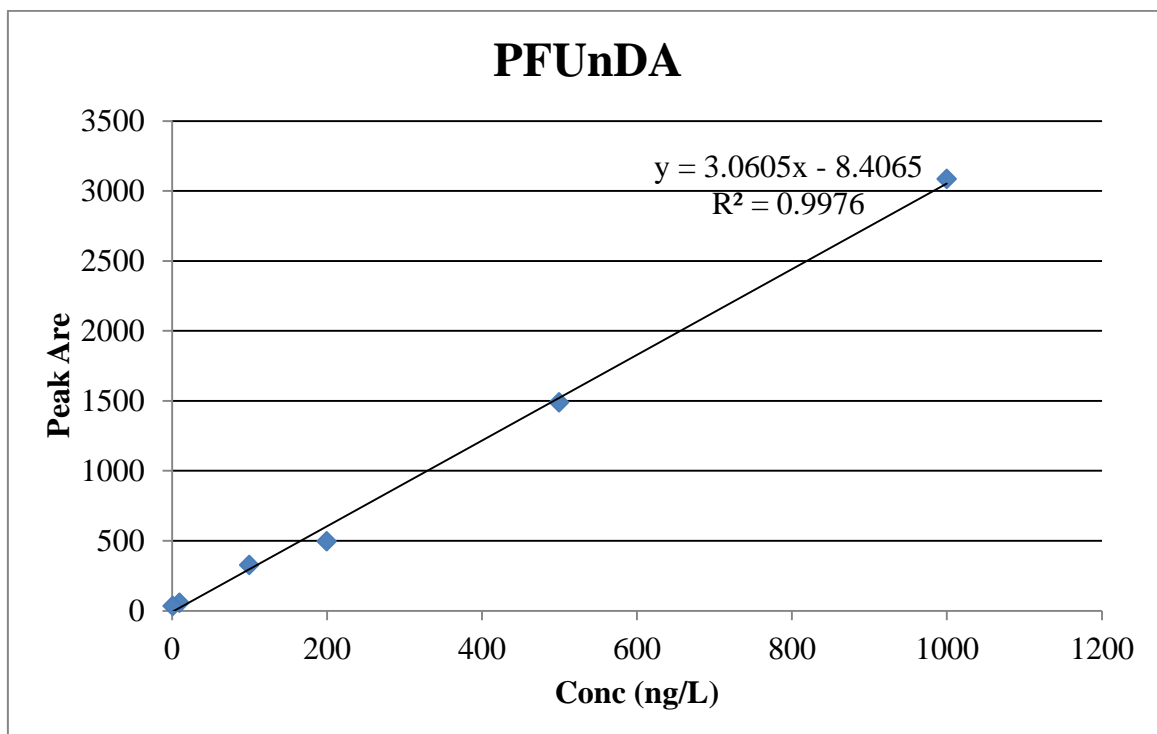
**Appendix H: Linear standard curve for perfluorooctane Sulfonate (PFOS)**



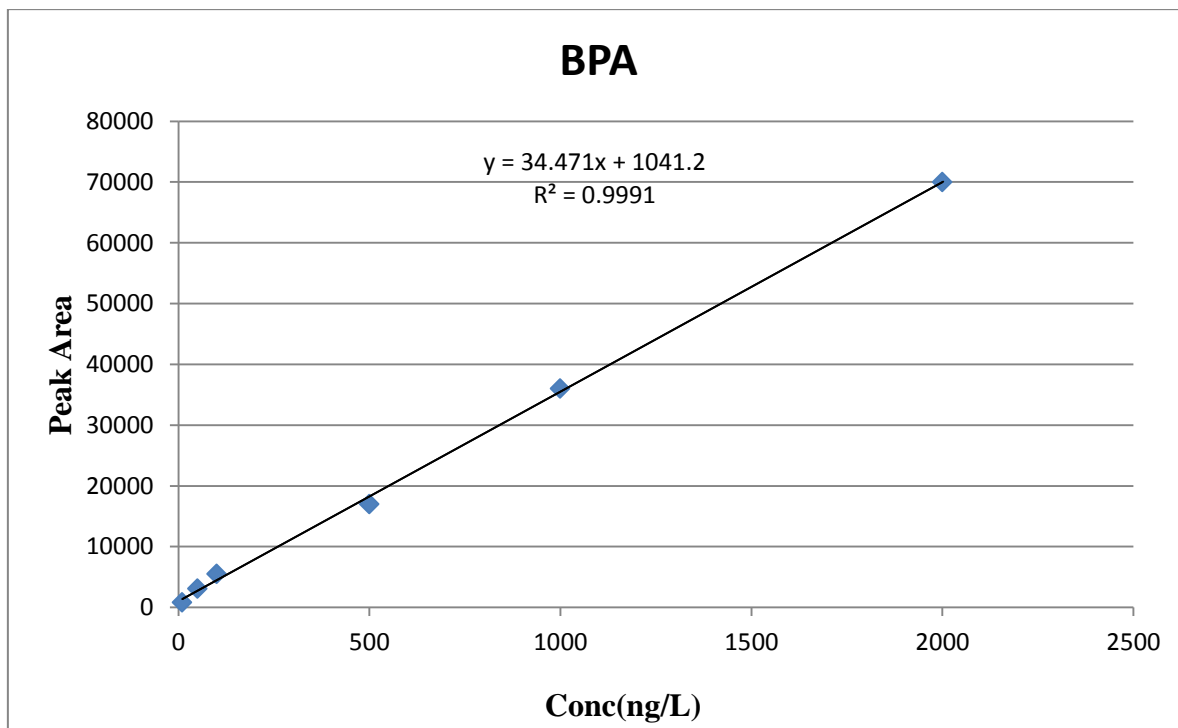
**Appendix I: Linear standard curve for perfluorodecanoic acid (PFDA)**



**Appendix J: Linear standard curve for perfluoroundecanoic acid (PFUnDA)**



**Appendix K: Linear standard curve for bisphenol A**



**Appendix L: Linear standard curve for Acetaminophen**

