Cape Peninsula University of Technology

PERFLUORINATED COMPOUNDS AND TRIHALOMETHANES IN DRINKING WATER SOURCES OF THE WESTERN CAPE, SOUTH AFRICA

by

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DECLARATION

I, **Xolelwa Booi**, declare that the contents of this thesis represent my own work, and that the thesis has not previously been submitted for academic examination towards any other qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology or the National Research Foundation of South Africa.

Signed **Date**

ABSTRACT

This study focused on quantifying two types of internationally regulated contaminants found in drinking water: 1) Trihalomethanes (THMs) and 2) Perfluorinated compounds (PFCs).

The first contaminants monitored were THMs, classified as a group of chemicals that are formed along with others during the disinfection of water using liquid chlorine, chlorine dioxide or chlorine gas. Hence, the resulting compounds are called disinfection by-products (DBPs). The disinfectant reacts with natural organic matter in water to form common THMs, which include chloroform ($CHCl_3$ or CF), bromodichloromethane ($CHCl_2Br$ or BDCM), dibromochloromethane ($CHClBr_2$ or DBCM) and bromoform ($CHBr_3$ or BF), with chloroform being the most common in chlorinated water systems. The current study has focused on THMs for two primary reasons: 1) THMs have raised significant concern as a result of evidence that associate their presence in drinking water with potential adverse human health effects, including cancer and 2) the levels of THMs in drinking water post-treatment is not monitored regularly in South Africa and thus far, there is inadequate and limited information about their concentration levels for drinking water treatment plants (DWTPs) and distribution stations (DWDSs) of the Western Cape, South Africa before, distribution to various suburbs, including townships. THMs normally occur at higher levels than any other known DBPs and their presence in treated water is a representative of the occurrence of many other DBPs.

THMs were quantified in chlorinated drinking water obtained from seven (7) DWTPs, namely; Atlantis, Blackheath, Faure, Brooklands, Steenbras, Voelvlei and Wemmershoek, and one DWDS in Plattekloof. This included determining THMs concentration in tap water collected from various suburbs including townships, to assist local authorities in obtaining information on their concentration and whether or not the presence of residual chlorine and organic matter on post-treatment results has increased THMs at the point of use.

THM analysis was performed using liquid-liquid extraction/gas chromatography with electron capture detector (LLE-GC-ECD) analytical process according to the EPA method 501.2, which was used with minor modifications. The instrument operational conditions were as follows: Column → DB5-26, 30 mm, 0.53 mm, 1.0 µm *d*f HP-1 (Agilent Technologies, USA); Carrier gas → Helium at a constant inlet pressure of 15 kPa; Make-up gas → 99.9% Nitrogen gas at 60 L/min; Injector temperature → 40°C; Oven temperature → 270°C and Detector temperature → 300°C. Since natural organic matter (NOM) in raw water is a precursor for THM formation, NOM analysis was performed as total organic carbon (TOC) using Spectroquant TOC test kits. Other drinking water quality parameters analysed were pH, residual free chlorine, conductivity and total dissolved solids (TDS).

The average Total THM concentrations detected from seven of the DWTPs, including the DWDS, ranged from 26.52 µg/L (for Plattekloof) to 32.82 µg/L (for Brooklands), with the observed concentrations being comparable. The average chloroform concentrations were the

highest in all the water samples, ranging from 11.74 µg/L (for Plattekloof) to 22.29 µg/L (for Voelvlei), while DBCM had the lowest concentration. The only DWTP that was not comparable with the seven DWTPs was Atlantis, with the highest average TTHM concentration of 83.48 µg/L and a chloroform concentration of 46.06 µg/L. From the tap water samples collected from 14 Western Cape suburbs, the average TTHM concentrations ranged from 5.30 ug/L (for Mandalay) to 13.12 µg/L (for Browns Farm, Philippi), and all these concentrations were lower than the TTHM concentrations detected in the water samples from the DWTP. Overall, the average total THM and individual THM species concentrations were below the recommended SANS 241:2011 and WHO drinking water guideline limits. This included the observed pH (6.39 to 7.73), residual free chlorine (0.22 to 1.06 mg/L), conductivity (121 to 444 µS/cm), TDS (93.93 to 344.35 mg/L) and TOC (0.38 to 1.20 mg/L). All these water quality parameters were within the specification limits stipulated in SANS 241. However, the average residual free chlorine concentration for Atlantis was very low (0.06 mg/L), which was below the WHO minimum residual free chlorine concentration guideline value of 0.2 mg/L for a distribution network – an indication that suggested the need for a re-chlorination station prior to distribution to households. Low chlorine content might result in the formation of unwanted biofilms in the distribution network, thus reducing the organoleptic properties of the water. Additionally, there was no direct link between several water quality parameters quantified (i.e. pH, TOC and water temperature) to TTHM formation. However, a high chlorine dose was observed to result directly in a higher concentration of chloroform in treated water prior to distribution.

The second contaminants monitored were Perfluorinated compounds (PFCs), which are non-biodegradable, persistent and toxic organic chemicals known for their ability to contaminate environmental matrices, including drinking water sources. In recent years, many researchers considered it essential to identify and quantify PFC levels in drinking water worldwide with the main focus being on the two most abundant PFCs; namely Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS). Their toxic effects to human health, plants and wildlife were also evaluated, classifying them as possible carcinogens. We know from the literature reviewed that, although the presence of PFCs in drinking water has been documented worldwide, there is limited information about their presence specifically in South African drinking water sources, even about less studied PFCs such as Perfluoroheptanoic acid (PFHpA), Perfluorododecanoic acid (PFDoA), Perfluorononanoic acid (PFNA), Perfluoroundecanoic acid (PFUA), Perfluorodecanoic acid (PFDeA) and the well-known PFOA including PFOS. Although several other PFCs have been detected in water sources and reported in various studies, the USEPA only issued drinking water guideline limits for Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS) of 400 ng/L and 200 ng/L, respectively, with no mention of the other PFCs. However, these PFCs have similar properties to those of PFOA and PFOS as they have been shown to impose similar detrimental health effects on human health. This study thus

focused on the detection of PFCs in both raw and treated drinking water in the Western Cape DWTPs such as Atlantis, Blackheath, Faure, Brooklands, Steenbras, Voelvlei and Wemmershoek, and one DWDS in Plattekloof.

Water samples (raw and treated water) used in this study for PFC analysis were collected in 2L polypropylene screw capped bottles. PFC analysis was performed in four sample batches for each location collected through the period of October to December 2012 (summer). PFCs were analysed in accordance with a modified EPA method 537, which entails solid phase extraction (SPE) followed by analysis using a liquid chromatography/tandem mass spectrometer (LC/MS/MS). The slight modification was with the water sample volume used for extraction, which was increased from 250 mL to 500 mL. The instrument used was an HPLC - Ultimate 3000 Dionex HPLC system and MS model - Amazon SL Ion Trap, with the following MS/MS operational conditions and Ion mode: MS Interface → ESI; Dry temp → 350°C; Nebulizing pressure → 60 psi; Dry gas flow → 10 L/min; Ionisation mode → negative; capillary voltage → +4500V; End plate offset → −500V while the separation column was a Waters Sunfire C18, 5 µm, 4.6 × 150 mm column (Supplier: Waters, Dublin, Ireland) with an operational temperature of 30°C.

From the results obtained in this study, seven different PFCs (i.e. PFHpA, PFDoA, PFNA, PFUA, PFDeA, PFOA and PFOS), were detected in raw and treated water with PFOA and PFOS being the least detected PFCs as they were detected only in raw water (PFOA) from Faure, as well as raw and treated water (PFOS) from Brooklands. The highest concentration observed in treated water was for PFHpA, which was quantified at a maximum average concentration of 43.80 ng/L (Plattekloof). The maximum average concentrations of other PFCs detected were as follows: PFDoA - 4.415 ng/L for Faure raw water; PFNA - 2.922 ng/L for Plattekloof outlet; PFUA - 7.965 ng/L for Brooklands treated water and PFDeA - 2.744 ng/L for Faure raw water. Another observation from the results was that the concentration of the majority of the PFCs detected in treated water was higher than that quantified in raw water, suggesting possible contamination by materials used during water treatment.

In conclusion, THMs detected in treated water from various DWTPs and one DWDS in the Western Cape met the required local and international drinking water quality guidelines, while the presence of PFOS, PFOA, PFHpA, PFDoA, PFNA, PFUA and PFDeA in treated water requires that local water professionals continue to monitor their presence to ensure that measures for their reduction are in place. Furthermore, the National standards (SANS 241) for municipal drinking water guidelines must be updated to include the monitoring of PFCs, including the lesser known and less studied PFCs such as PFHpA, PFDoA, PFNA, PFUA and PFDeA.

DEDICATION

To my beautiful daughter

Sphesihle Neo Linomtha

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I am eternally grateful to the following:

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BIOGRAPHICAL SKETCH

Xolelwa Booi was born in Cape Town on 30 December 1984 and grew up in the Eastern Cape, Keiskammahoek at Rabula Location. She attended Emmangweni Primary School and later attended St Matthews High School in Keiskammahoek, where she matriculated with distinction in 2001. In 2002 she enrolled at Cape Peninsula University of Technology (then known as the Cape Technikon) for a National Diploma in Chemical Engineering, which she was awarded (*cum laude*) in 2004. In 2005 she enrolled for BTech in Chemical Engineering, which she also passed (*cum laude*). She enrolled for a *Magister Technologiae* degree in 2010 under the direct supervision of Dr. Karabo Ntwampe and co-supervision of Prof. Marshall Sheldon and Dr. Sebusi Odisitse. Her research was based on the analysis of Perfluorinated compounds and Trihalomethanes in drinking water sources of the Western Cape. She is currently working at Eskom, Koeberg Nuclear Power Station, in the Western Cape.

LIST OF OUTPUTS

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

Manuscripts submitted for publication still under review:

Identification and Removal of Perfluoroalkyl compounds in Water Sources of the Western Cape, South Africa.

Submitted abstracts:

Are Perfluorinated compounds, PFOA and PFOS, a threat to human health in South Africa? A case study of their worldwide presence in drinking water (*Submitted for a poster on Research day at Cape Peninsula University of Technology*).

LAYOUT OF THESIS

The overall aim of the study was to quantify Trihalomethane concentrations in chlorinated drinking water and to evaluate the presence of Perfluorinated compounds (PFCs) from the several drinking water treatment works and distribution stations of the Western Cape, South Africa. The references are listed at the end as a separate chapter in accordance with the Harvard method of referencing.

The thesis is subdivided into the following chapters:

- **Chapter 1**, the introduction, provides the background on THMs and PFCs. It also presents research questions to be addressed by the study, lists the overall objectives and clearly states topics that were not covered by the study.
- **Chapter 2**, the first literature review chapter, provides a summary of background studies performed on THMs, their origin, precursors, factors affecting their formation, and their routes into human bodies including toxic effects and treatment methods. It also presents a detailed literature review on the existence of PFCs worldwide, their sources and routes to human bodies, their toxicity to humans, other living organisms and possible treatment methods.
- **Chapter 3**, the second literature review chapter provides information on drinking water quality guidelines, highlighting maximum allowable limits for both THMs and PFCs in various countries.
- **Chapter 4**, the research methodology chapter, summarises the modified EPA 501.2 used for THM analysis. Information on sampling sites, sampling frequency, and sample collection procedures are discussed as well as the materials and methods used for analysing PFCs, as listed in method 537 of the EPA.
- **Chapter 5** is the results and discussion chapter.
- **Chapter 6**, overall discussion and conclusion chapter, presents answers to each of the research questions listed in Chapter 1 while also listing recommendations for future research.

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GLOSSARY

ABBREVIATIONS

ACS	American Chemical Society
AMW	Apparent Molecular Weight
BDCM	Bromodichloromethane
BOM	Biodegradable Organic Matter
CCT	City of Cape Town
$CHCl_3$	Chloroform (CF)
$CHCl_2Br$	Bromodichloromethane (BDCM)
$CHClBr_2$	Dibromochloromethane (DBCM)
$CHBr_3$	Bromoform (BF)
DBCM	Dibromochloromethane
DBPs	Disinfection By-products
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DPD	Diethyl-p-phenylene diamine (for chlorine testing)
DWA	Department of Water Affairs
DWDS	Drinking Water Distribution Stations
DWTP	Drinking Water Treatment Plants
ECD	Electron Capture Detector
FAs	Fulvic Acids
FDA	Food & Drug Administration
GAC	Granular Activated Carbon
GC	Gas Chromatography
H_2SO_4	Sulphuric acid
HAs	Humic Acids
HLB	Hydrophilic-lipophilic balance
HPLC	High Performance Liquid Chromatography
HPV	Health-based Precautionary Value
HS	Humic Substances
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantification
MIEX	Magnetic Ion Exchange Resin
MLD	Minimum Levels of Detection
MS	Mass Spectrometry

MTBE	Methyl tert-butyl ether
NaOH	Sodium Hydroxide
NOM	Natural Organic Matter
P&T	Purge & Trap
PAC	Particulate Organic Matter
PAV	Precautionary Action Values
PFAA	Perfluoroalkyl Acids
PFASs	Perfluoroalkyl sulfonates
PFCs	Perfluorinated Chemicals/Compounds
PFDeA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate
PFHpA	Perfluoroheptanoic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane Sulfonate
PFUA	Perfluoroundecanoic acid
RF	Response Factor
RRF	Relative Response Factor
SABS/SANS	South African Bureau of Standards/South African National Standards
SPE	Solid Phase Extraction
TDS	Total Dissolved Solids
TFP	Trihalomethane Formation Potential
THMs	Trihalomethanes
TTHMs	Total Trihalomethanes
TOC	Total Organic Carbon
TOX	Total Organic Halides (X-I,Cl,Br,F)
USEPA	United States Environmental Protection Agency
UV_{254}	Ultra-violet absorbance capacity at 254 nm
VOCs	Volatile Organic Compounds
WHO	World Health Organisation

TERMS AND DEFINITIONS

Biodegradation: is the chemical breakdown of materials by a physiological environment.

Breakpoint chlorination: all chlorine reacts with any organic materials present in water until they are destroyed. Chlorine then reacts with amino acids or urea to form chloramines. If more chlorine is added, the chloramines are then broken down until there is nothing left to react. At this point, chlorine appears as residual free chlorine and this point is referred to as 'breakpoint'.

Disinfection: a chemical process used in water systems, in which chemicals are added to inactivate or kill pathogens found in water.

Disinfection by-products (DBPs): a group of chemicals formed when chlorine or other disinfectant reacts with naturally occurring organic matter in water.

Drinking water sources: sources of water from fresh or bulk water treatment works that are distributed to households for the purpose of general household use or ingestion. This includes river water and water sources that can be used for either household applications or agricultural purposes.

Genotoxic chemicals: chemicals which are capable of causing damage to DNA. These chemicals may bind directly to DNA or act indirectly leading to DNA damage by affecting enzymes involved in DNA replication. Such damage can potentially lead to the formation of a malignant tumor, but DNA damage does not necessary lead inevitably to the creation of cancerous cells.

Hydrolysis: is decomposition of a chemical compound by reaction with water, such as the dissociation of a dissolved salt or the catalytic conversion of starch to glucose.

Internal Standard (IS): a pure chemical added to an extract or standard solution in a known amount and used to measure the relative response of other analytes and surrogates that are components of the same solution. The internal standard must be a chemical that is structurally similar to the method analytes, has no potential to be present in samples, and is not a method analyte.

Organoleptic: relating to the senses (taste, sight, smell, touch).

Perfluorocarbons (PFCs): also known as Perfluorinated surfactants (PFSs), these are a class of organofluorine compounds that have all hydrogen atoms replaced with fluorine atoms on a carbon chain. Examples include: 1) Perfluorooctane sulfonate (PFOS) and 2) Perfluorooctanoic acid (PFOA) which are widely used as fluorosurfactants in various industrial applications.

Toxicological studies: Studies on the health effects from exposure to high dosages of contaminants usually involving animals in a laboratory.

Trihalomethanes (THMs): chemical compounds in which three of the four hydrogen atoms of methane (CH_4) are replaced by halogen atoms. These are a group of four chemicals that are formed when chlorine, used to control microbial contaminants in drinking water, reacts with naturally occurring organic and inorganic matter in water.

Volatile Organic Chemicals: synthetic chemicals dissolved in water, which vaporise at low temperatures.

CHAPTER 1

INTRODUCTION

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INTRODUCTION

1.1 Background

As water plays a major role in our lives, our water resources must be managed in a manner that ensures its sustainability. South Africa is a country that regularly faces water shortages especially in townships and rural areas. A study by Smith (2001) predicted that with the current rate of water consumption, the existing system of water supply is likely to run-out within a few decades. Additionally, the quality of water, whether intended for drinking or irrigation, is of significant importance to human health worldwide, in both developed and developing countries. The state of water quality can have a major impact on human health when it is not managed properly, as poor quality water can result in outbreaks of water-borne diseases. Accordingly, many countries have developed treatment processes to eliminate these water-borne diseases such as cholera and dysentery as these have led to high mortality rates, especially in children under the age of 5 years, the elderly and the immunocompromised. Over a century, disinfection processes have been introduced for water treatment. Disinfection through inactivation usually involves the use of disinfectants such as chlorine, ozone and chlorine dioxide, and a combination of chlorine and ammonia (chloramines) rendering many of these organisms inactive, except for protozoa such as *Cryptosporidium* and *Giardia*, which have been found to be resistant to chlorine disinfection. This has necessitated the use of UV radiation. UV disinfection technology is of growing interest in the water industry since it was demonstrated that UV radiation is very effective against (oo)cysts of *Cryptosporidium* and *Giardia*, two pathogenic micro-organisms of major importance for the safety of drinking water (Hijnen *et al.,* 2006). Different disinfectants produce different types and concentration of disinfection by-products (DBPs) for which regulations have been established for drinking water. DBPs include trihalomethanes (THMs), haloacetic acids, bromates and chlorites.

Chlorination of drinking water is presently the most common, cost effective, reliable, and convenient procedure used for water treatment worldwide. However, despite the effectiveness of chlorine in preventing mortality from water-borne pathogens, there is a concern about possible adverse health effects associated with chronic exposure to DBPs (Freese & Nozaic, 2004; Do *et al.*, 2005). Chlorine reacts with naturally occurring organic matter, such as humic and fulvic acids, in raw water to produce a variety of DBPs, the most common being trihalomethanes (THMs), haloacetic acids and haloacetonitriles. The most abundant DBPs that have been studied in detail are the THMs: 1) chloroform or trichloromethane ($CHCl_3$); 2) bromodichloromethane ($CHCl_2Br$); 3) dibromochloromethane

($CHClBr_2$) and 4) bromoform or tribromomethane ($CHBr_3$), with the chloroform being by far the most common in most water systems (Do *et al.*, 2005; Hasan *et al.*, 2010).

All the other DBPs are equally important but the focus for the current study was on THMs, as significant concern has been raised as a result of evidence showing their association, with potential adverse human health effects including cancers, such as pancreatic and bladder cancer (Do *et al.*, 2005) and also adverse reproductive effects including developmental effects (Reif *et al.*, 1996). Furthermore, THMs occur at higher levels than any other known DBPs and their presence in treated water is representative of the occurrence of many other chlorination DBPs (EPA Stage 2 Rule Fact sheet, 2005).

Since the discovery of chlorination/disinfection by-products in drinking water in 1974, numerous toxicological studies have been conducted showing the carcinogenicity of DBPs in laboratory animals (including bromates, certain trihalomethanes and haloacetic acids) (USEPA, ICR, 17 August 2011). However, despite thorough scientific research, no conclusive evidence has ever proven that THMs, in quantities at which they occur in drinking water, are harmful to humans (Freese & Nozaic, 2004). As a result of this inconclusive evidence, both the International Agency for Research on Cancer (IARC) and the World Health Organisation (WHO) have concluded that there is not enough evidence to prove that THMs pose a health risk (Government of Western Australia Fact sheet, 2009). On the other hand, USEPA believes that the weight of evidence presented by the available epidemiological studies on chlorinated drinking water and toxicological studies on individual DBPs does in fact support a potential hazard concern and warrant regulatory action (USEPA, ICR, 17 August 2011). Consequently, municipal and national government authorities should make every effort to maintain concentrations of all DBPs as low as reasonably achievable, without compromising the effectiveness of the disinfection process. To honour this, many government agencies, such as the United States Environmental Protection Agency (USEPA), have mandated regular assessment of THMs for public water systems (USEPA, 2009).

In December 1998, the EPA established the Stage 1 Disinfectants/Disinfection By-products Rule that requires public water systems to use treatment measures to reduce the formation of DBPs, in order to meet specified standards, such as the total trihalomethanes (TTHMs) limit of 100 µg/L, which was later reduced to 80 µg/L in 2001 (USEPA, ICR, 17 August 2011). The Canadian and the Romanian drinking water guidelines for TTHMs are set at 100 µg/L (Ristoiu *et al.*, 2009). In South Africa, the acceptable drinking water quality is governed by the SABS, which issues drinking water specifications for different parameters as found in SANS 241. The maximum allowable limit for TTHMs specified in SANS 241:2005 is 200 to 300 µg/L for a maximum period of 10 years and the limit specified in SANS 241:2011 for individual THM species is 60 µg/L for bromodichloromethane (BDCM), 100 µg/L for

dibromochloromethane (DBCM) and bromoform, and 300 µg/L for chloroform. This SANS limit is high for species that are suspected to cause potential health effects, particularly chloroform, raising questions as to whether or not the limit was set based on thorough research, taking into account that the USEPA has reduced the limit from 100 to 80 µg/L. In South Africa, THM formation has been studied in the North West, Free State, KwaZulu Natal, Gauteng and Northern Cape provinces – see Figure 1.1, with the exception being the Limpopo, Eastern Cape, Mpumalanga and Western Cape provinces (Nothnagel *et al.*, 2008).

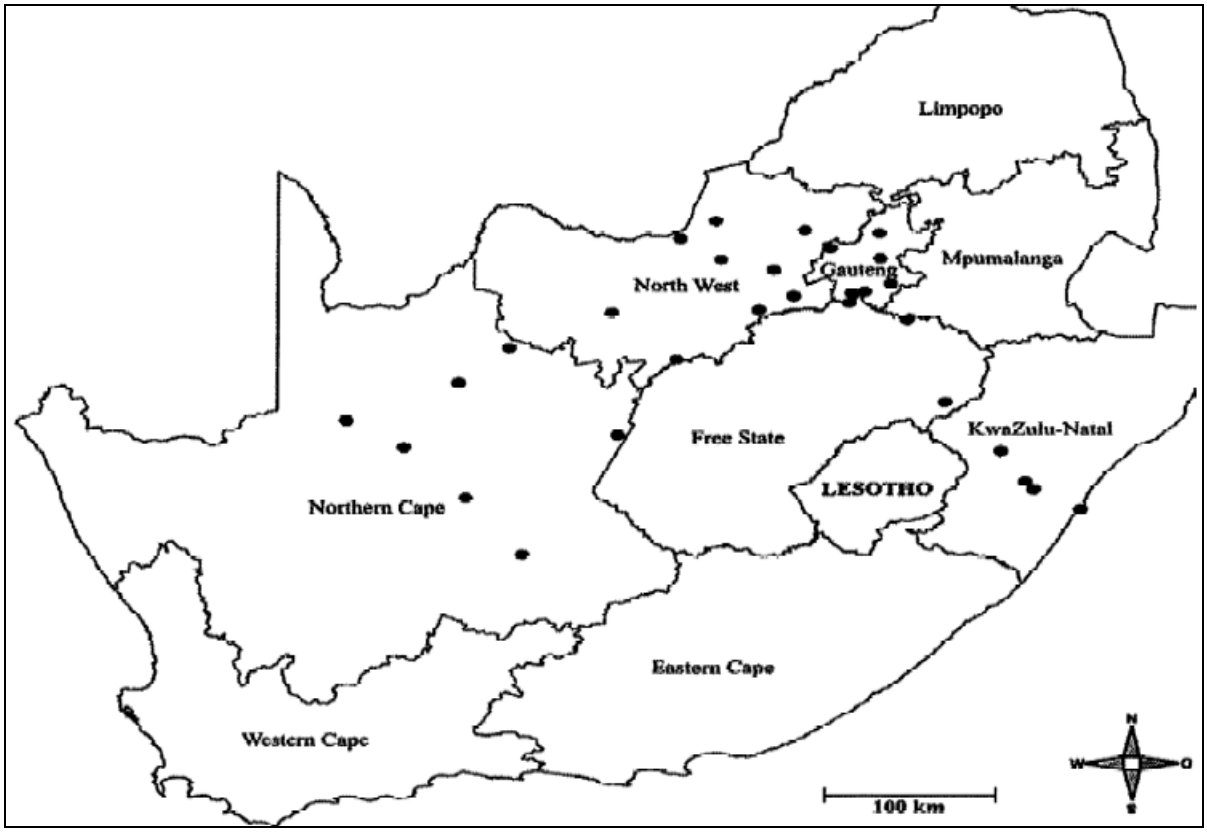


Figure 1-1: Sampling sites for THM analysis across South Africa

THMs are not the only organic contaminants of concern for regulatory agencies monitoring treated drinking water quality. Another contaminant class of concern is Perfluorinated compounds (PFCs). Perfluorinated compounds (PFCs) are persistent, bio-accumulative and toxic fluorine-based chemicals (Skutlarek *et al.*, 2006). PFCs do not occur naturally, they are used in man-made fluorinated compounds in consumer and industrial applications (Joensen *et al.*, 2009). In other words, they are synthetic organic compounds and have been manufactured worldwide since the 1950s. They are present in the environment because they are used in various manufacturing processes for items such as textiles, clothes, carpets, cosmetics and fire-fighting foams (Jin *et al.*, 2009). The common route of exposure to humans is through the consumption of PFC-contaminated water and foods (Ericson *et al.*, 2008; Strynar *et al.*, 2009). As water usage and consumption is the

basis of everyday human activity and as a result of the resistance of the PFOA and PFOS to hydrolysis, biological breakdown and metabolism by microorganisms due to the strength of the carbon-fluorine bonds; these fluorine-based organic compounds can be ingested, thus bio-accumulate in the body (Takagi *et al.*, 2008).

Several studies have been done worldwide with results showing widespread presence of PFCs in the environment: for example, they have been detected in environmental and tap water (Ericson *et al.*, 2009; Jin *et al.*, 2009; Post *et al.*, 2009); in human semen (Joensen *et al.*, 2009); and in human sera (Hanssen *et al.*, 2010; Hölzer *et al.*, 2008; Oliaei *et al.*, 2006; Skutlarek *et al.*, 2006; Steenland *et al.*, 2009). Furthermore, high levels of PFC contamination have been detected in various media globally, such as in drinking water, sediment from landfills and living organisms (Oliaei *et al.*, 2006) and in food (Clarke *et al.*, 2010). However, in South Africa, the study of PFC contamination in drinking water sources has never been reported, except that perfluorinated compounds were detected for the first time in maternal serum and cord blood of pregnant women at 1.6 ng/mL for perfluorooctane sulfonate (PFOS) and 1.3 ng/mL for perfluorooctanoic acid (PFOA) (Hanssen *et al.*, 2010).

Based on the results obtained from various PFC contamination studies, some countries determined a need to develop regulatory limits as guidelines for acceptable PFC levels in drinking water for human consumption, based on their potential human health effects (Rumsby *et al.,* 2009). There is limited existing national legislation that defines specific limit values for all PFCs, particularly in South Africa. In 2009, the USEPA issued drinking water provisional health advisory, but only for PFOA and PFOS, with a maximum limit of 400 ng/L and 200 ng/L for both compounds, respectively (USEPA, 2009). However, in South Africa, PFC regulation is non-existent and therefore devoid of regulatory guidelines. The SABS (SANS 241), which governs drinking water quality, issued drinking water specifications for the different parameters as found in SANS 241: 2005. Microbial, physical, organoleptic, and chemical safety requirements were all specified in the guidelines with no mention of any of the perfluorinated chemicals (PFCs). Prior to the 2010 FIFA World Cup, the Department of Water Affairs and Forestry (DWAF) conducted audits on the drinking water quality management evaluations to comply with current Blue Drop Certification requirements. During the audit, common microbiological and chemical analyses were performed, but with no mention of PFCs as analytes (Blue Drop Certification, 2010). In addition, the new SANS 241:2011 still did not have guidelines for any PFCs. The question that arises from this information is that if PFCs have been proven toxic and detrimental to human health, what must be done in South Africa to closely monitor PFC contamination and prevalence in order to implement treatment strategies and thus preserve the quality of our already scarce water resources.

As a result of this alarming void in regulations which governs the maximum PFC limits in South Africa, the greatest concern is that the South African population may be unknowingly exposed to high levels of PFCs via drinking water. As these compounds are water soluble, conventional water treatment systems and processes may not eliminate these compounds completely (Takagi *et al.*, 2008). From the reviewed literature, more than 70% of the published research primarily reports on the two abundant PFCs, namely PFOA and PFOS, with much less attention given to other perfluorinated compounds. Furthermore, although other PFCs have been studied and detected in water sources by some researchers, the USEPA only issued drinking water guideline limits for PFOA and PFOS, with no mention of other PFCs. However, other PFCs have the same properties as PFOA and PFOS and therefore it is logical to hypothesise that they have the same detrimental health effects to humans as PFOA and PFOS. This study focused on the detection of several other PFCs in drinking water sources of the Western Cape, including PFOS and PFOA.

The overall aim of this research was to determine whether these PFCs are present in drinking water sources in concentrations exceeding the USEPA guideline limits. Since no study on either THMs or PFCs was reported in the Western Cape, the current study focuses on quantifying these contaminants in the Western Cape's drinking water, with an extensive focus on treatment works with a theoretical treatment capacity exceeding 100 ML/day. Furthermore, THMs were investigated in various suburbs including townships to determine whether residual chlorine further reacts with NOM in treated water, thus increasing THMs at the point of use, i.e. at household water taps. This included the determination of residual chlorine at several distribution points to assess whether there is a need for re-chlorination at these points.

1.2 Research questions

The following questions were addressed:

- Are there Trihalomethanes (THMs) and Perfluorinated compounds (PFCs) in the water sources of the Western Cape?
- What are the levels of THMs in treated drinking water distributed to various households in the Western Cape, particularly at the point of use?
- Since a country such as South Africa is devoid of studies to determine the presence and extent of PFC contamination in drinking water sources, what are the actual levels of PFCs in treated drinking water distributed to reservoirs used to supply household water?

- Are the current treatment methods sufficient to completely eradicate PFCs and natural organic matter, a precursor for trihalomethanes, from raw water intended for human consumption?
- Are the levels of THMs and PFCs so alarmingly high in drinking water sources of the Western Cape, that it is critical to implement treatment methods in order to reduce these levels?
- Are the levels of THMs and PFCs within the USEPA or South African guidelines?

1.3 Objectives of the research

The primary objectives of this study were as follows:

- To determine the physico-chemical characteristics of the source (raw) water, i.e. water quality parameters, which influence and/or contribute to THM formation.
- To quantify concentration levels of THMs: chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$), in chlorinated drinking water from different drinking water treatment plants (DWTPs) with a treatment capacity exceeding 100 ML/day and a drinking water distribution station (DWDS).
- To correlate total THMs to physico-chemical characteristics, i.e. pH, total organic carbon, etc., of the raw water.
- To assess whether chlorine levels are at required levels at DWTPs/DWDS prior to distribution and to correlate chlorine dose to chloroform concentrations as it is the main DBP for chlorinated water.
- To determine total THM levels at the point of use, i.e. in various suburbs and townships; and
- To identify and quantify the concentration levels of perfluorinated compounds in raw and treated water.

1.4 Significance of the research

PFC contamination has been detected in drinking water and in human bodily fluids of individuals drinking contaminated water worldwide, but alarmingly in South Africa, the presence of these compounds in drinking water is undocumented and therefore unknown. This study provided information about the prevalence of perfluorinated compounds contamination in both drinking water and raw water in the Western Cape, South Africa. In addition, THMs have been detected in high levels in other provinces of South Africa; no data exists from the Western Cape for treatment systems that utilise chlorine as a disinfectant. The data generated can therefore assist in comprehending the prevalence of THMs and PFCs in treated water and enhancing monitoring mechanisms regionally.

1.5 Delineation of the research

This study did not cover the following:

- Sources of PFCs in the DWTP/DWDS studied.
- PFC and THM concentration levels in drinking water sources of other South African provinces.
- Analysis of other types of DBPs such as haloacetic acids and haloacetonitriles; bromates, etc.
- Reduction of THMs and PFCs in the collected water; and
- Influence of seasonal variations on THMs and PFCs presence in the water.

CHAPTER 2

TRIHALOMETHANES AND PERFLUORINATED COMPOUNDS

CHAPTER 3

DRINKING WATER QUALITY GUIDELINES FOR TRIHALOMETHANES AND PERFLUORINATED COMPOUNDS

LITERATURE REVIEW

CHAPTER 2
TRIHALOMETHANES AND PERFLUOROCARBONS IN DRINKING WATER

2.1 Trihalomethanes

2.1.1 Sources of drinking water

Trihalomethanes are not expected to be found in raw water but are present in chlorinated water, when chlorine, used as a disinfectant, reacts with naturally occurring organic matter (NOM), such as humic and fulvic acids. For the purpose of this study, the water for THM analysis was obtained from seven drinking water treatment plants (DWTPs): Blackheath, Voelvlei, Steenbras, Faure, Wemmershoek, Brooklands including Atlantis, and at one drinking water distribution station (DWDS) at Plattekloof.

2.1.2 Precursors of Trihalomethanes

Trihalomethanes are formed when chlorine is added as a disinfectant to water containing organic matter. Such organic matter, which are precursors of THMs, include humic and fulvic acids, organic substances (such as amino acids) and bromide ions (Yamada *et al.,* 1998). A variety of organic compounds (THM precursors) may exist in dissolved, colloidal or particulate forms in water supplies. Humic substances constitute the major fraction of organic matter and THM precursors in most water supplies (Yamada *et al.,* 1998). The following are the known precursors of THMs in surface waters during chlorination: humic substances, amino acids, aliphatic compounds, bromide and iodide ions.

(i) Humic substances as precursors of Trihalomethanes in drinking water

Humic substances are the product of decaying organic matter. They are components of humus and they come from the accumulation and natural chemical reaction of by-products from the degradation of organic matter. They are commonly present in soils, surface water, sewage, compost heaps, marine and lake sediments. Humic substances are generally considered as a series of relatively high molecular weight compounds, brown to black coloured substances formed by secondary synthesis reactions. There are three types of humic substances, which differ slightly in acidity and chemical composition. They are humic acids, fulvic acids and humin (Pettit, 2006).

Humic acids (HAs) - comprise a mixture of weak aliphatic (carbon chains) and aromatic (carbon rings) organic acids, are not soluble in water under acidic conditions but are soluble in water under alkaline conditions and consist of humic substances fraction that is precipitated from aqueous solution when the pH is below 2. HAs are the major extractable component of soil humic substances with their molecular weight ranging from 10 000 to 100 000 (Pettit, 2006).

Fulvic acids (FAs) – are a mixture of weak aliphatic and aromatic organic acids, soluble in water at all pH conditions. The size of fulvic acids is smaller than that of humic acids, with molecular weights ranging from approximately 1000 to 10 000. FAs have an oxygen content twice that of HAs. In addition, they have many carboxyl (-COOH) and hydroxyl (-OH) groups, and therefore fulvic acids are much more chemically reactive. The exchange capacity of FAs is more than double that of HAs due to the total number of carboxyl groups present (Pettit, 2006).

Humins – are that fraction of humic substances, which are not soluble in water at any pH. Humin complexes are considered macro-organic (very large) substances because their molecular weights range from approximately 100 000 to 10 000 000 (Pettit, 2006)

Figures 2.1 and 2.2 offer graphic illustrations of the differences in the structures of both humic and fulvic acids.

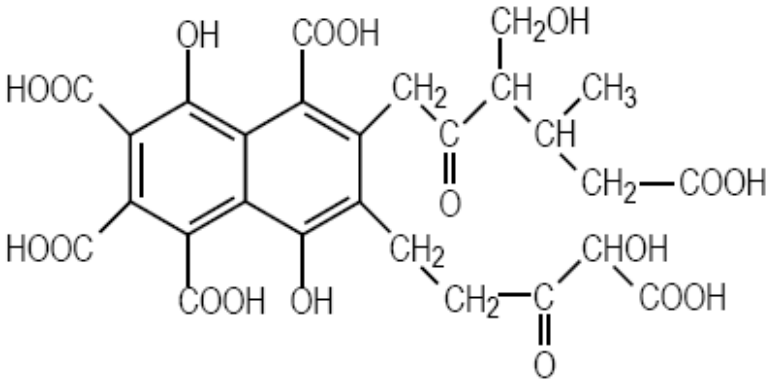


Figure 2-1: Model structure of fulvic acids, courtesy of Zadow, 2009

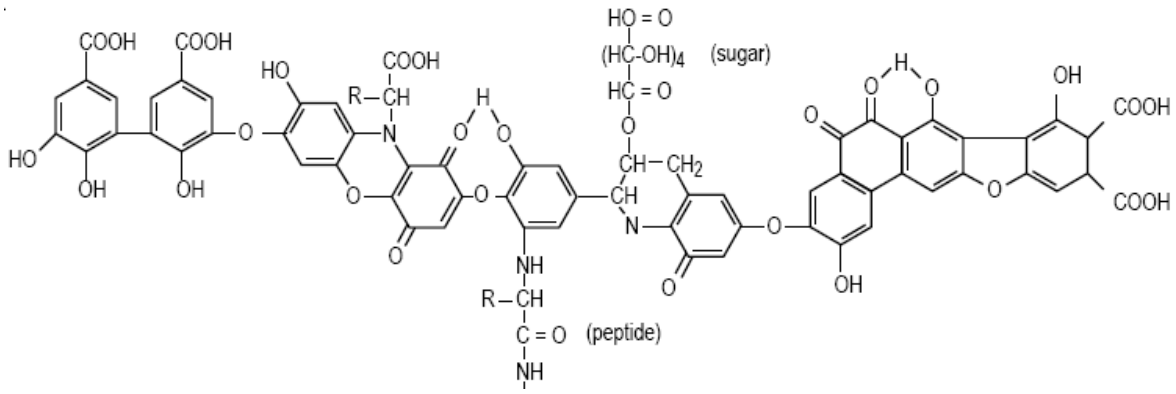


Figure 2-2: Model structure for humic acids, courtesy of Zadow, 2009

A study by Yamada *et al.* (1998) found that fulvic acids were predominant in most rivers, with the range of fulvic and humic acids in river water being 0.50 to 3.2 mg/L and 0.025 to 0.2 mg/L, respectively. These results showed that the concentrations of fulvic acids were about 10-times more when compared to humic acids. In addition, the concentrations of humic substances were showed to be consistently higher in summer and low in winter. This may have been due to an increase in the water temperature and microbiological activity, which cause the biological conversion of organic matter present in water and soils into humic substances and to an increase in the solubility of humic substances during warmer seasons. This also means that THM concentration is likely to be higher in summer than in winter months (Yamada *et al.*, 1998).

(ii) Amino acids as precursors of Trihalomethanes during chlorination

Amino acids are molecules containing an amino group, a carboxylic group, and a side chain specific to each amino acid. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen atoms (Figure 2.3).

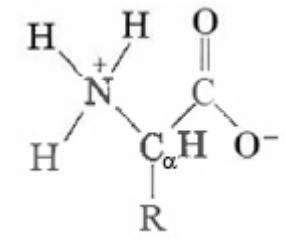


Figure 2-3: The generic structure of an alpha amino acid in its unionised form, courtesy of Seager *et al.,* 2010

In a study by Hong and co-workers, amino acids were chlorinated and examined for the formation of THMs and HAAs, and it was reported that the amino acids exhibited a high chlorine demand but low THM formation (Hong *et al.*, 2009).

(iii) Aliphatic compounds as precursors of Trihalomethanes during chlorination and bromination

Aliphatic compounds are compounds containing carbon and hydrogen atoms (also known as aliphatic hydrocarbons) connected in either straight, branched, non-aromatic chains or rings. The possibility of aliphatic compounds as THM precursors after chlorination and bromination in controlled laboratory-scale batch experiments was assessed by Dickeson's group, and four beta-dicarbonyl acid compounds were found to be important precursors for the formation of THMs, such as chloroform and bromoform, after 24 hours at a pH of 8 (Dickenson *et al*., 2008) – a pH value observed for most drinking water.

(iv) Bromide and iodide ions as precursors of Trihalomethanes

Bromide and iodide ions can have an effect on the formation and speciation of DBPs during chlorination. In natural waters, whereby various levels of bromide and iodide ions are present, molar yields of THMs increased with an initial increase in bromide concentration. However, total organic halogen (TOX) concentrations decreased substantially with increasing initial iodide concentrations. Furthermore, the extent of iodine substitution was found to be much lower than that of bromine substitution. This is because some of the iodide was oxidized to iodate by chlorine and as a result of this oxidation, an increase in chlorine doses resulted in reduced levels of iodinated organic by-products (Hua *et al*., 2006). These findings indicate that bromide is the most definite precursor of THMs as compared to iodine. Chlorine, being a stronger oxidizer than bromine or iodine, displaces bromine from bromides and iodine from iodides, as indicated in Eq. 2.1 and 2.2 (The group 17 elements, 26 June 2012):

$$Cl_2 + 2\ Br^- \rightarrow 2\ Cl^- + Br_2 \qquad (2.1)$$

Similarly:

$$Cl_2 + 2\ I^- \rightarrow 2\ Cl^- + I_2 \qquad (2.2)$$

2.1.3 Factors influencing Trihalomethane formation in drinking water treatment plants

As trihalomethanes are formed when chlorine used as a disinfectant in drinking water, reacts with natural organic matter (NOM), there are several factors that influence THM formation during disinfection. In studies conducted by Ristoiu *et al.* (2009) and Chowdhury and Champagne (2008), several factors were identified as influencing THM formation during water treatment: chlorine dose, presence of the natural organic matter in raw water, disinfection reaction/dosing time, raw water temperature and its pH. Each of all these factors need to be considered and quantified when analysing THMs in treated water.

(i) Chlorine dose

During THM analysis and laboratory kinetic experiments on Romanian raw water, it was observed that the main parameter influencing THM formation was the chlorine dose used. The higher the chlorine dose, the higher the chloroform ($CHCl_3$) concentrations (Ristoiu *et al.*, 2009).

(ii) Natural organic matter (NOM)

Similarly, NOM which includes humic substances, hydrophilic acids and other dissolved organic materials originating from soil and biological processes in the water can cause an increase in THM formation. These organic materials react with chlorine during disinfection processes to form THMs. For example, the results obtained showed a correlation between NOM and the concentration of $CHCl_3$ after chlorination, i.e. an increase in NOM increases the raw waters THM formation potential (Ristoiu *et al.,* 2009; Yamada *et al.*, 1998). In fact, NOM is considered the most important precursor of THMs formation; however, there is limited information on specific or direct measurement of NOM and because of this, NOM can be expressed in terms of surrogate measures, such as total organic carbon (TOC), dissolved organic carbon (DOC) or UV absorption capacity at 254 nm (UV_{254}). In this present study NOM was quantified as TOC (Ristoiu *et al.,* 2009; Yamada *et al.*, 1998).

(iii) Reaction time

Although significant quantities of THMs form rapidly after chlorine addition, i.e. on site at the DWTP, there is ample evidence that they increase in concentration along the water delivery chain, especially in cases where there is a high concentration of residual chlorine in the water. Additionally, an extended reaction time can also contribute to increased levels of THMs in drinking water, with the rate of formation decreasing after the rapid reaction phase (Chowdhury & Champagne, 2008). For example, increasing the reaction time increased the $CHCl_3$ concentration (Figure 2-4). The results showed that $CHCl_3$ production increases with an increase in chlorine concentration and contact time (Ristoiu *et al.*, 2009; Chowdhury & Champagne, 2008).

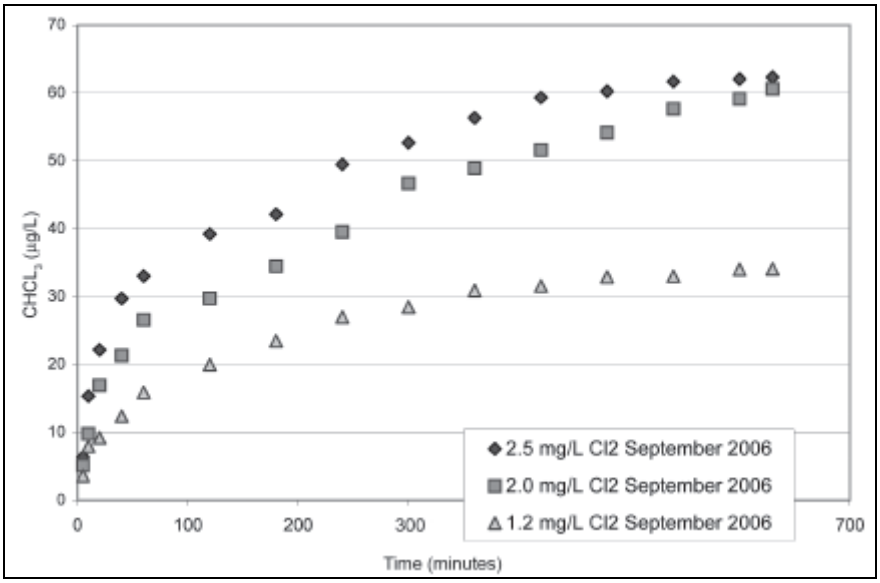


Figure 2-4: $CHCl_3$ formation rate with increasing chlorine doses and reaction time (Ristoiu *et al.*, 2009)

(iv) Water temperature

THM formation has been shown to be temperature dependent. During winter, for example, THM formation was slower due to lower water temperatures and in summer months the concentration increased with a difference of ~50%. This could be due to the fact that the chlorine demand was lower in winter than in summer (Yamada *et al.*, 1998; Ristoiu *et al.*, 2009).

(v) Water pH

A study was conducted by Ristoiu and co-workers, in which the pH of treated water was adjusted by the addition of 0.5M NaOH or 0.1M H_2SO_4 in order to evaluate the effect of pH on THM formation. It was observed that when the pH was in the range between 6.5 and 7.9, 10 to 25% more of THMs were formed than under any other pH range (Ristoiu *et al.*, 2009). Furthermore, THM formation increased significantly with an increase in pH; however, at a higher pH (pH>8), hydrolysis of haloacetic acids and haloacetonitriles takes place, leading to lower total organic halides in treated water, thus THMs (Chowdhury & Champagne, 2008).

2.1.4 Natural Organic Matter reduction in raw water prior to chlorination reduces disinfection by-products

One way of reducing THMs in treated water is by reducing precursors, NOM in particular (Eikebrokk & Juhna, 2006). NOM is an abundant constituent of all drinking waters, and is known to affect the coagulation process. It may also interfere with adsorption and disinfection processes. NOM in water is a major concern and should be removed from raw water for a number of reasons, as it:

- affects organoleptic properties of water (colour, taste and odour);
- reacts with most disinfectants used in water treatment, thus reducing their disinfection power;
- influences disinfectant demand, and disinfection process design, operation and maintenance;
- produces disinfection by-products (DBPs) of various kinds;
- influences heavily on coagulant demand; and
- fouls membranes (Eikebrokk & Juhna, 2006).

Various processes such as enhanced coagulation and flocculation, MIEX (magnetic ion-exchange resin) treatment, activated carbon filtration and nanofiltration can remove NOM. Bond *et al.* (2010) reported that: (1) coagulation, (2) coagulation and MIEX anion exchange resin and (3) nanofiltration can remove NOM and reduce the bulk dissolved organic carbon (DOC) as shown in Table 2-1.

Table 2-1: Comparison between the NOM removal processes (Bond *et al., 2010*)

Treatment process	THM precursors removal	Bulk DOC reduction
Coagulation	15 - 34%	7 - 44%
Coagulation-MIEX anion exchange resin	60 - 79%	46 - 72%
Nanofiltration	66 - 92%	67 - 94%

This shows that using either nanofiltration or the MIEX process in combination with coagulation can improve THM precursor removal as compared to using coagulation alone. The principal characterisation of the MIEX process is related to the hydrophobicity of the resins where NOM in water is fractionated into hydrophobic and hydrophilic components by the resin, resulting in high molecular weight (HMW) components in NOM attaching to functional groups in the resin while nanofiltration removes a large number of HMW compounds which form a major part of NOM (Croue *et al.*, 2000 cited in Bond *et al.*, 2010).

(i) Enhanced coagulation and flocculation

Coagulation and flocculation is one of the important unit processes in most water and advanced wastewater treatment plants. Their objective is to enhance the separation of particulate species in downstream processes such as sedimentation and filtration. Colloidal particles and other finely divided matter are brought together and agglomerated to form larger sized particles that can be subsequently removed in a more efficient manner. Coagulation has been shown to be an effective process for the removal of many other contaminants that can be adsorbed by colloidal metals, toxic organic matter, viruses and radionuclides. Coagulants are added into water to neutralise charges on dispersed non-settleable solids such as clay and colour-producing organic substances. Once the charge is neutralised, the small suspended particles are capable of sticking together forming microflocs. The water surrounding the newly formed microflocs should be clear, if it is not, coagulation has to be carried to completion by adding more coagulant (Wang *et al.*, 2005).

Contrary to conventional coagulation processes primarily aimed at turbidity removal, enhanced coagulation employs the use of elevated coagulant dosages and strict control of pH. The implications of this shift in treatment targets and operating conditions include elevated sludge production rates, increased solids load to subsequent separation processes (i.e. settling, flotation and/or filtration units), use of inorganic acids for pH control, increased focus on operational and optimisation issues, possible conflicts in optimum conditions for various target parameters like turbidity, NOM and reduction of micro-organisms. In addition, coagulated NOM will form loose flocs and lead to early filter breakthroughs, i.e. shortened filter runs compared with conventional coagulation and filtration processes for the removal of turbidity (Eikebrokk & Juhna, 2006).

(ii) MIEX (magnetic ion-exchange resin) treatment for natural organic matter removal

The MIEX® (Magnetic Ion Exchange resin - MIEX® is a registered trademark of Orica Australia Pty Ltd) process, jointly developed by the Australian Water Quality Centre, Orica Water Care and CSIRO, has been designed specifically for the removal of dissolved organic carbon (DOC) from drinking water. The very small particle size of the resin, ~150 µm (outer diameter) provides a high surface area allowing rapid adsorption kinetics of DOC. The negatively charged DOC is removed by exchanging with a chloride ion on active sites on the resin surface. The magnetised component assists in the resin recovery process (Morran *et al.*, 1996; Slunjski *et al.*, 1999 cited in Cook *et al.*, 2001).

During a laboratory study conducted by Cook *et al.* (2001), of conventional alum treatment versus MIEX® treatment from two water reservoirs, Hope Valley and Myponga (selection based on the differences in the character of their DOC), the removal of natural organic matter using MIEX® for DOC removal showed the following:

(a) Removal of DOC under optimised treatment conditions using alum and MIEX® combined was very similar to MIEX® alone and much better than conventional or enhanced coagulation with alum. For instance, combined treatment (alum and MIEX®) removed 2.3 and 1.4 times the DOC removed by enhanced coagulation with alum from the Hope Valley and Myponga, respectively.

(b) Treatment with MIEX® alone resulted in a much greater removal of compounds which were less than 2000 apparent molecular weight (AMW) compared with the alum treatment. However, unlike alum treatment, there were compounds greater than 2000 AMW remaining after MIEX® treatment.

(c) Combining the alum with MIEX® resulted in a significant reduction of UV absorbing compounds above and below 2000 AMW.

(d) The character of the DOC of the treated water was the same regardless of whether MIEX® was used prior to or after alum dosage.

(e) Including MIEX® in the treatment stream reduced the chlorine decay and THM formation. Using MIEX® alone or combined with alum, the amount of chlorine consumed was 50 and 80 % less of that obtained with conventional alum treatment (after 60 minutes) (Cook *et al.,* 2001).

These laboratory tests showed that, incorporating MIEX® in the treatment process can improve DOC removal, resulting in lower chlorine use and THM formation (Cook *et al.*, 2001).

(iii) Activated carbon filtration for organic matter removal

The size, number and chemical structure of organic acid molecules depends on many factors including raw water pH and temperature. Because of these factors, removing organics can be difficult and site-specific. Granular activated carbon (GAC) is also commonly used for removing organic constituents and residual disinfectants in water supplies. The two principal mechanisms by which activated carbon removes contaminants from water is by adsorption and catalytic reduction, i.e. organics are removed by adsorption and residual disinfectants by catalytic reduction (DeSilva, 2000).

Generally, adsorption takes place because all molecules exert forces to adhere to each other. Activated carbon adsorbs organic material because the attractive forces between

the carbon (non-polar) and the contaminant (non-polar) are stronger than the forces keeping the contaminant dissolved in water (DeSilva, 2000).

2.1.5 Properties of Natural Organic Matter

NOM is a chemically complex and heterogeneous mixture of organic substances produced from decay processes. It may have distinctive characteristics associated with its origins, i.e. vegetation, soil, wastewater and agricultural return. For example, dissolved organic matter (DOM) from aquatic algae has a relatively large nitrogen content and low aromatic carbon and phenolic contents. On the other hand, terrestrially derived DOM has relatively low nitrogen content but large amounts of aromatic carbon and phenolic compounds. Thus, the aromatic content, believed to be a major reactive component, varies with different sources. The contribution of each carbon source is seasonally dependent, and the hydrological and biogeochemical processes involved in physical mixing and in the carbon cycles can alter the chemical composition and the physical structure of DOM (Eikebrokk *et al.*, 2006).

NOM can be broadly divided into two fractions: humic substances (HS) and non-humic substances (non-HS) which include carbohydrates, lipids, and amino acids. HS are considered resistant to bacterial degradation, whereas non-humic substances are biodegradable and often referred to as biodegradable organic matter (BOM). NOM is divided into dissolved organic carbon (DOC) and particulate organic carbon (PAC). DOC is defined operationally as material that passes a 0.2- or 0.45 µm filter. DOC consists of truly dissolved substances and macromolecules with colloid-like properties, especially humic substances. PAC is defined as material that is captured by a 0.2 or 0.45 µm filter. PAC consists of larger particles like algae, bacteria, and particulate detritus. In addition, PAC includes inorganic particles covered by NOM (Eikebrokk *et al.*, 2006).

Table 2-2 below summarises the impact of specific organic fractions and their ability to form DBPs, promote biofilm growth, their role in corrosion in distribution systems and their impact on aesthetic quality of drinking water (Montreuil, 2011).

Table 2-2: Impact of specific organic fractions on their ability to form disinfection by-products and their impact on aesthetics in drinking water (Montreuil, 2011)

Organic fraction	Chemical compounds	DBP Formation potential	Biological activity	Transport of metals	Colour	Taste and odour
Hydrophobic neutral (HON)	Hydrocarbons, Pesticides, Carbonyl compounds, aldehydes, ketones, alkyl alcohols	Moderate	High	Low	None	None
Hydrophobic acid (HOA)	Humic and fulvic acids, aromatic acids, high Mw carboxylic acids, phenols	High	Low	High	High	Moderate
Hydrophobic base (HOB)	Aromatic amines, proteins, amino acids, amino-sugars	Moderate	High	Moderate	High	None
Hydrophilic acid (HIA)	Sugar acids, fatty acids, hydroxyl acids, low Mw carboxylic acids	n/a	n/a	n/a	n/a	n/a
Hydrophilic base (HIB)	Polysaccharides, aromatic amines, proteins, amino acids, amino-sugars	Moderate	High	Moderate	High	None
Hydrophilic neutral (HIN)	Oligosaccharides, polysaccharides, aldehydes, ketones, low Mw alkyl alcohols	n/a	n/a	n/a	n/a	n/a

2.1.6 Reduction methods for Trihalomethanes

To maintain these acceptable levels, chlorinated water should be further treated to reduce the THM levels. Methods to reduce THM concentrations in chlorinated drinking water include but are not limited to the following:

- Aeration at the tap - aeration is the process by which air is circulated through, mixed with or dissolved in a liquid or substance. Aeration of chlorinated water will assist in dispelling any dissolved chlorine gas including volatile THMs.
- Allowing treated water to stand or by passing it from one container to another a few times before drinking.
- Boiling the water for one minute and allowing it to cool before drinking; and

- Using activated carbon water filters (Government of Western Australia, 2009).

Activated carbon is carbon, which has a slight electro-positive charge added to it, making it an effective adsorbent for organic chemicals and impurities. As the water passes over the positively charged carbon surface, the negative ions of the contaminants are drawn to the surface of the carbon granules. Activated carbon filters used for home water treatment typically contain either granular activated carbon (GAC). Although both are effective, carbon block filters generally have a higher contaminant removal ratio compared to GAC. Important factors affecting the efficiency of activated carbon filtration are the amount of carbon in the unit and the amount of time the contaminant spends in contact with the carbon. Similarly, the lower the flow rate of the water, the more time the contaminants will be in contact with the carbon, resulting in increased absorption. The advantage of using activated carbon filters is that they offer an effective removal process for organic compounds including volatile organic compounds (VOCs), radon, and chlorine including cancer-causing THMs, and are very cost effective (Home water purifiers and filters, 2011, Homewaterpurifiers.com, 26 September 2011).

The disadvantages are that with granular activated carbon (GAC), it requires scheduled filter replacements to eliminate the possibility of 'channelling', which reduces the contact between the contaminant and the carbon, reducing the efficiency of the filter. Additionally, frequent carbon filter changes are often required which can be costly (Home water purifiers and filters, 2011, Homewaterpurifiers.com, 26 September 2011).

In addition, reducing natural organic matter that produces disinfection by-products prior to chlorination can control the formation of THMs. Since chlorine is the most popular and effective disinfectant, it is imperative to reduce as much organic matter as possible before chlorination. This can be done by coagulation in combination with other methods such as nanofiltration, which will reduce the bulk DOC (Bond *et al.,* 2010). Although treatment processes such as plain filtration (rapid sand, slow sand) and post chemical coagulation are commonly used in South Africa, this in effect does not reduce sufficient quantities of NOM to reduce THM formation. Other alternatives include using ion-exchange, ozonation and advanced oxidation processes. The use of some of these processes, such as ozonation, can lead to elevated bromate concentrations through oxidation of bromide present in the water. Chlorination is largely preferred and widely used in South Africa due to its affordability and acceptability as a suitable option for most municipalities and for DWTPs in developing countries (WHO, 2011).

2.1.7 Toxic effects of Trihalomethanes to humans

Trihalomethanes have been detected worldwide in all water with natural organic matter treated with chlorine but there is no conclusive evidence that they are harmful to human health. However, THMs have been shown to cause cancer in laboratory animals and are classified as Group B carcinogens, for which epidemiological studies conducted, revealed that they affect reproductive health and cause developmental effects (Reif *et al.*, 1996). There was also evidence of an increased risk of pancreatic cancer (Do *et al*., 2005) and reduction in the menstrual cycle length, thus negatively affecting ovarian function (Windham *et al.*, 2003). The difficulty in providing conclusive evidence for an association between exposure to DBPs and cancer in humans lies both in inherent characteristics related to toxicity of these compounds and in issues regarding the epidemiological methods used. Epidemiological studies have focused on THMs because they are carcinogenic in experimental animals and they are the most prevalent DBPs in most chlorinated drinking waters (Kogevinas, 2011).

The USEPA has stated that there is a possibility of an increased risk of bladder cancer over a lifetime of drinking water with THMs above 80 µg/L, but this risk occurs only after decades of drinking water with elevated THMs. The USEPA also concluded that as long as exposure to DBPs such as chloroform remains under given threshold values that cause cell damage, the risk of cancer is very low (USEPA, 1998). As THMs do not pose as high a health risk as compared to waterborne diseases and as a result of this inconclusive evidence, both the International Agency for Research on Cancer and the World Health Organisation have concluded that there is not enough evidence to prove that THMs pose a health risk (Government of Western Australia, 2009).

2.1.8 Routes of Trihalomethanes into the human body

The source of most chlorination DBPs is treated drinking water; hence, the most common route of THMs into human bodies is through the consumption of chlorinated water. The following are common routes of THMs into human bodies:

- Drinking chlorinated (disinfected) water- oral ingestion.
- Consuming food prepared with THM-containing water.
- Inhaling some of the THMs as they are volatile and may easily vaporise into air during bathing in showers, and
- Absorption through skin while showering, bathing, or swimming (Government of Western Australia, 2009).

While the above-mentioned routes are the common routes, this does not exclude other routes of THMs into human bodies that potentially exist.

2.2 Perfluorinated compounds

2.2.1 Perfluorinated compounds detection in drinking water sources

In the introduction to the current study, it was made clear that perfluorinated compounds are abundant throughout the environment worldwide. Because they are used in various consumer and industrial applications worldwide, their spread is inevitable. In a study by Steenland *et al.* (2009), research results indicated that adults: (1) who reside near a chemical plant using PFCs, (2) who consume local produce and (3) who drink well water near the contaminated source, had high concentration of PFCs in their blood compared to other age groups.

In a recent study, perfluoroalkyl and polyfluoroalkyl substances (PFASs) classified as PFCs, were detected in mineral water (n_{pfc} = 10) and tap water (n_{pfc} = 19). The highest concentration (total PFASs) detected in tap water was 42.7 ng/L The maximum tolerable daily intake was only calculated for PFOA and PFOS, while the other PFCs were not considered (Gellrich *et al.*, 2012). Furthermore, in another study by Boiteux *et al.* (2012), several PFCs (n_{pfc} = 10) were detected in raw and treated drinking water samples. Of these, the highest individual PFC concentrations detected in the raw water was 139 ng/L for perfluorohexanoic acid (PFHxA). PFOS, PFOA and perfluorohexane sulfonate (PFHxS) were the predominant PFCs; however, only PFOS and PFOA had their health-based guidelines values listed in the study. Similarly, PFOS, PFOA and perfluorononanoic acid (PFNA) were detected in paired maternal and cord serum samples ($n_{samples}$ = 237) collected between 1978 and 2001 in Southern Sweden. PFOS, PFOA and PFNA were higher in maternal serum (15, 2.1, 0.24 ng/L, respectively) than in cord serum (6.5, 1.7, 0.20 ng/L, respectively). Although PFNA was detected in low concentrations, its health-based guideline value was not listed (Ode *et al.,* 2013).

From the literature reviewed, it is clear that although PFOSs and PFOAs are the most abundant and most studied PFCs, other PFCs are also detected both in water sources and from human sera (Hanssen *et al.*, 2010; Hölzer *et al.*, 2008; Oliaei *et al.*, 2006; Skutlarek *et al.*, 2006; Steenland *et al.*, 2009). Since PFCs have similar properties, health-based guideline values must also be determined for other PFCs.

2.2.2 Sources of Perfluorinated compounds in the environment

PFCs do not occur naturally in the environment, they are either released to the environment by anthropogenic activities or are released via sewage wastewater treatment plants or even as a result of breakdown of other PFCs (Joensen *et al.*, 2009, Oliaei *et al.*, 2006). In a study in Minnesota, Oliaei *et al.* (2006) reported that PFCs were manufactured and later released to various environmental matrices such as landfills, wastewater treatment facilities and rivers. Some of the PFC-containing products manufactured by the Minnesota's 3M company (Minnesota Mining and Manufacturing) eventually breakdown into PFOS and PFOA, which are classified as persistent organic pollutants (POP's). Due to widespread presence and long-term risks associated with PFOS, the production of PFOS-related PFCs by the 3M Company has since been discontinued. The concern is that even with the discontinuation of PFCs, PFC-containing products (for commercial, consumer and industrial applications) are still being utilised worldwide in different forms, contributing to environmental deterioration and contamination (Oliaei *et al.,* 2006).

A study by Harada *et al.* (2003) showed river water downstream from a sewage plant to be highly contaminated with PFOS. Similarly, a PFOA contamination study was also conducted in a community surrounding a chemical plant utilising PFOA (Steenland *et al.*, 2009). Residents residing closely to the chemical plant, in particular, those growing and consuming their own vegetables and using well water for irrigation, showed high prevalence of PFOA in their sera. Furthermore, those who were working at the chemical plant showed much higher levels of PFOA in their serum (~309% increase in PFOA) compared with individuals residing in a nearby residential area who had never worked at the plant (Steenland *et al.*, 2009).

Another study by Murakami *et al.* (2009) suggested that street runoff and wastewater could be possible sources of PFCs in rivers. The concentrations of PFCs in street runoff were hypothesised to be derived from street dust near major traffic routes as a result of vehicular residue. The study also concluded that perfluorinated surfactants concentrations increased during wastewater treatment due to possible degradation of PFC precursors. Once more, concentrations of perfluorinated surfactants in street runoff were equal to or higher than those in wastewater influents and secondary effluents, suggesting that street runoff potentially contaminates aquatic environments with perfluorinated surfactants.

Furthermore, the concentration of PFOS and PFOA in urban areas was significantly higher than those in remote areas (Murakami *et al.,* 2009). Summarised PFC sources are listed in Table 2-3.

Table 2-3: Summary of PFC sources, manufacturers and processes and the region in which they were detected in the environment

Source of PFCs	Environmental effects	Country Region	Reference
PFC manufacturing company (3M)	3M manufactured a group of PFCs, which were later released to the environment and result in contamination of various environmental matrices.	Minnesota	(Oliaei *et al.*, 2006)
Downstream of a sewage plant	The sewage plant upstream of the Tama river discharges PFOS contaminated water to the river. This resulted in the contamination of the river water with PFOS.	Japan	(Harada *et al.*, 2003)
Areas surrounding a chemical plant	Individuals working at the plant, residing near the chemical plant, consuming contaminated water and locally cultivated agricultural produce showed high levels of PFOA contamination because of the high exposure to PFOA.	Ohio	(Steenland *et al.*, 2009)
Street runoff and waste water	Street runoff derived from street dust or running vehicles and waste water were deemed possible sources of PFCs.	Japan	(Murakami *et al.*, 2009)
Downstream of urban areas	Urban activities such as operation of fluorochemical industries were proven a source of contamination to rivers (water sources) downstream of the areas.	China	(Jin *et al.*, 2009)

2.2.3 Treatment methods for Perfluorinated compound (removal from water)

High concentration levels of PFCs have been detected in drinking water sources worldwide, raising concern as it detrimentally affects human health. Guideline values for drinking water have been recommended based on studies by various researchers (Rumsby *et al.,* 2009); however, these values can be controlled and kept to a minimum if there are treatment methods in place. Various methods have been assessed for PFC absorption using: zeolites, sludge, activated carbons, resin, non ion-exchange polymers and granular activated carbon. For the current study, granular activated carbon will be discussed briefly.

(i) Treatment methods for water and wastewater containing perfluorocarbons

(a) Granular activated carbon (GAC) filtration

Granular activated carbon is commonly used for removing organic contaminants and residual disinfectants in water supplies. Activated carbon is a favoured water treatment technique because of its multifunctional nature and because it does not leave residue which might affect the quality of the treated water (DeSilva, 2000). However, the performance of activated carbon is affected by factors such as molecular weight of the contaminants, pH, particle size, flow rate and temperature. Briefly, the effects are as follows:

- As the **molecular weight** of the contaminant increases, the activated carbon used effectively adsorbs the compounds to be removed because the molecules are least soluble in water.
- **pH** – most organic compounds are less soluble and more readily adsorbed at a lower pH, hence for effective adsorption, a rule of thumb is to increase the size of the carbon bed by twenty percent for every pH unit above neutral (pH = 7).
- The **flow rate** is inversely proportional to the rate of adsorption, i.e. the lower the flow rate the longer the contact time thus improved adsorption; and
- The higher the **temperature** the lower the solution viscosity which will achieve a higher diffusion and adsorption rate. However, in certain instances, the adsorption depends on the organic compound being removed as higher temperatures can disrupt the adsorptive bond and thus slightly decrease adsorption (DeSilva, 2000).

Most activated carbons are made from raw materials such as nutshells, wood, coal and petroleum-based product residues. Principal mechanisms by which activated carbon removes contaminants from water are adsorption and catalytic reduction, i.e. organic contaminants are removed by adsorption and residual disinfectants by-products are removed

by catalytic reduction. Activated carbon's adsorptive properties facilitate the removal of organic compounds (DeSilva, 2000).

In a study by Oliaei *et al.* (2006), wastewater was treated with granular activated carbon (GAC) prior to removing PFCs. The GAC treatment system represents the best method available for removal of most organic compounds, including PFCs, from wastewater effluents. After treatment using GAC the PFOS levels were reported to have dropped from 24800 ng/L to 1330 ng/L over a one year period and PFOA levels dropped from 7760 ng/L to 1670 ng/L. This represents a 95% reduction PFOS and a 79% reduction in PFOA through the activated carbon system. Other PFCs were also detected (as shown in Table 2-4) with PFBS (perfluorobutane sulfonate) being detected at the highest concentration after GAC treatment. The PFBS concentration also increased from 26100 ng/L before treatment to a concentration of 169000 ng/L after GAC treatment. This increase, which has been observed in other PFCs - as shown in Table 2-4, is not currently justified as experimental errors may have occurred (Oliaei *et al.*, 2006).

Table 2-4: PFC levels in Influent and Effluent at the 3M Cottage Grove (Minnesota) Wastewater Treatment Plant (WWTP) (Oliaei *et al.*, 2006)

PFCs	GAC influent (ng/L)	GAC effluent (ng/L)
PFBA	100000	58100
PFPeA	2350↑	3130↑
PFHxA	2100↑	3760↑
PFHpA	<1240	1090
PFOA	7760	1670
PFOS	24800	1330
PFNA	<1330	<884
PFDA	<1280	<855
PFUnA	<1270	<847
PFDoA	<1260	<842
PFBS	26100↑	169000↑
PFHxS	10000	1160
PFOSA	<1240	<825

From the concentration levels reported in Table 2-4, it was evident that the granular activated carbon (GAC) system was effective at reducing the concentration of PFOA and much more effective at reducing the concentration of PFOS in the wastewater. However, from this study alone, it is difficult to conclude that the activated carbon treatment system is effective in removal of carboxylic acids because PFOA and other PFCs were not removed

efficiently on a consistent basis, although the system did work well to remove PFOS at a 95% removal rate (Oliaei *et al.*, 2006). This is directly related to adsorbate and adsorbent molecular forces, which included the affinity of the GAC towards specific PFCs.

(b) Adsorption as an effective process for organic compound removal from water

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent. Adsorption occurs when the attractive forces between the carbon surface (non-polar) and the contaminant (non-polar) are stronger than the forces keeping the contaminant dissolved in water (polar), that is, it occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid. The specific capacity of the GAC to adsorb organic compounds is related to molecular surface attraction, the total surface area available per unit weight of carbon and the concentration of contaminants in the wastewater (Carbtrol, 1992; DeSilva, 2000).

2.2.4 Toxic effects of perfluorinated compounds to humans and animals

(i) Toxic effects of perfluorocarbons to human health

PFCs are extremely persistent and are not easily metabolised in animals and humans. Once PFCs enter the environment they are often bio-available and may enter the food chain, thus can be transferred from one medium to another such as from water to edible products (Oliaei *et al.*, 2006), after which they are ingested, accumulating in the human body. In a study by Joensen *et al.* (2009), effects of perfluoroalkyl compounds were examined in humans to ascertain their influence on the quality of semen in adult males. The results showed that serum with high concentrations of perfluoroalkyl acids (PFAAs) had significantly reduced numbers of normal spermatozoa. In addition, the spermatozoa concentration, total count, and motility were lower in men with high PFAA levels (.

In Minnesota, a mortality study on workers at the 3M plant, which operated for a 30-year period, showed a statistically significant association between PFOS levels in workers' blood with the development of bladder cancer. The analysis indicated that workers employed in high exposure areas were 13 times more likely to die of bladder cancer than the general population. Similarly, a retrospective mortality study showed a statistically significant association between prostate cancer mortality and employment duration in a PFOA manufacturing company. Cholesterol and triglyceride levels were positively associated with PFOA exposures as well [increase/decrease] in thyroid hormone (T3) in the exposed workers (Oliaei *et al.*, 2006).

Fei *et al* (2008) investigated effects of both PFOA and PFOS on foetal growth. PFOA and PFOS were measured in maternal blood samples taken early in pregnancy. The results showed that maternal PFOA levels in early pregnancy were associated with smaller abdominal circumference and birth length. To be specific, each ng/ml increase in PFOA resulted in a 0.069cm decrease in birth length and a 0.059cm decrease in abdominal circumference. Conversely, maternal PFOS levels were not associated with any of the foetal growth indicators. In contrast to Fei's findings, Apelberg *et al.* (2007) found minimal association between either PFOS or PFOA concentrations and newborn length or gestational age. Furthermore, both PFOS and PFOA were negatively associated with birth weight and size. These findings, i.e. the lack of association between PFOA exposure and gestational age, were however confirmed by Nolan *et al.* (2009).

In summary, because of the discrepancies in these findings, more research is required to confirm the observations reported and thus definitive conclusions. It is also quite possible that there were some shortcomings with these studies, such as small sample size and analytical methods with a detection limit above the PFC concentration likely to be present. It may also be that the analytical methods used were inconsistent, such as methodology development and design, demographic variations of the studied population and the magnitude of the exposure measured (Olsen *et al.*, 2009). More investigative work on epidemiologic research is required to address all the shortcomings and differences in order to generate consistent and reliable results. In addition, as can be clearly seen from the literature reviewed, these studies only focused on the health effects of PFOS and PFOA, neglecting the fact that all PFCs have similar properties and the health effects imposed by these two abundant PFCs might be imposed, to a lower or even higher degree, by the other PFCs. Future studies should therefore focus on all the PFCs.

(ii) Evidence of toxic effects of perfluorocarbons to living organisms

Numerous studies have been conducted on various living organisms to determine the toxicity of PFCs, as explained below. Animal studies by Oliaei *et al.* (2006) showed that PFOS is readily absorbed orally and is distributed mainly to the liver and blood with no further metabolism being observed, hence its bio-accumulation in living organisms. PFOS showed moderate toxicity to the liver in rats, adverse effects in monkeys such as anorexia and diarrhoea, post-natal deaths, and other developmental effects in rats offspring's exposed to low PFOS doses and prenatal developmental effects on rats and rabbits exposed to slightly higher PFOS doses.

PFOA has been proven to be a possible carcinogen in rats, inducing liver tumours (Oliaei *et al.*, 2006). Cui *et al.* (2009) also observed abnormal behaviour and sharp weight loss in male rats exposed to high doses of PFOS for 28 days. The study also confirmed the toxic effects of PFOS and PFOA in the liver and kidney, whereby the highest PFOS and PFOA levels were detected, indicating that the liver, kidney, and lungs might serve as repository organs for PFCs.

In another study by Huang and co-workers (2010), toxicity following exposure to PFOS was evaluated in zebrafish embryos. The embryos were exposed to various PFOS concentrations ranging from 0 to 8 mg/L from 6 to 120 hours post-fertilisation (hpf). PFOS was developmentally toxic in all stages of development and accumulated in the zebrafish embryos with minimal elimination. PFOS-induced cell death at 24 hpf was consistently observed in the brain, eye and tail region of embryos. Embryos exposed to PFOS showed various morphological malformations such as bent spine and uninflated swim bladder, had decreased heart beat rate, altered spontaneous movement and increased cellular death. Embryos/larvae at later developmental stages were found to be more sensitive to PFOS than those at earlier stages (Huang *et al.*, 2010).

These studies clearly showed that PFCs could negatively affect living organism development – observations that can also be applied to humans as well.

(iii) Evidence of toxic effects of perfluorocarbons to plants

Toxicity of PFOS and PFOA has been evaluated in plants. These compounds are carried over from the soil to the plants as the plants grow. Various crop plants were studied and they showed visible abnormalities at soils with certain PFOS/PFOA concentrations of 0.25 to 50mg/kg. Most crops grown on PFOS/PFOA contaminated soils showed visible abnormalities such as necrosis (premature death of cells and living tissues) in potatoes and oats, yellow colour in rye grass and diminished growth in potatoes and spring wheat at concentrations between 10 and 50mg/kg PFOS/PFOA. No toxic effects were observed in maize at any concentration (Stahl *et al.*, 2009).

In addition, toxic effects of PFOS on wheat were investigated with results showing that at low PFOS concentration (<10 mg/L), growth of wheat seedlings was stimulated and synthesis of chlorophyll and soluble protein induced. However, at higher PFOS concentrations greater than 10 mg/L, inhibition in elongation and biomass of roots and leaves was observed, leading to damage of the chlorophyll accumulation and soluble protein synthesis (Qu *et al.*, 2010).

2.2.5 Routes of perfluorinated compounds into human bodies

The presence of PFCs in humans can be confirmed by the monitoring of these chemicals in human sera. Some researchers have persuasively stated in their studies that the major transport of PFCs to humans, is through ingesting contaminated food and water or using materials containing PFCs on a regular basis (Skutlarek *et al.*, 2006). Ericsson *et al.* (2008) performed a study on the presence of PFCs in various food items, and the consumption of such food items. The study clearly stated that the outcomes obtained do not justify dietary intake as the main route of exposure, but that a variety of routes can contribute to the presence of PFC in humans. An additional study was performed, whereby foodstuffs were randomly purchased in Spain and a total of 36 composite samples corresponding to 18 different food groups were analysed. PFOS and PFOA were both detected. What was important to note was that a correlation between dietary intake and blood levels of PFOS was established (Ericson *et al*., 2008).

Similarly, Hölzer *et al.* (2008) found that consumption of contaminated tap water was directly proportional to the PFOA concentrations in blood plasma of humans. The higher the daily tap water intake, the higher the PFOA plasma levels. In addition, consumption of contaminated locally grown fruits and vegetables and fish caught from local lakes had a direct relation to the plasma PFC concentration in the local population (Hölzer *et al.,* 2008). This in particular makes drinking water a plausible major route of PFCs into the human body, as tap water can be used in numerous household activities. Therefore, a major focus of this study will be to quantify the type and concentrations of PFCs in drinking water in the Western Cape, South Africa.

CHAPTER 3
REGULATION OF TRIHALOMETHANES AND PERFLUOROCARBONS IN DRINKING WATER

3.1 Drinking water quality guidelines

3.1.1 Standards and analytes in other countries compared to South Africa

3.1.1.1 Acceptable limits for Trihalomethanes

The disinfection by-products, specifically THMs, are considered harmful to public health. As a result, health institutions worldwide have established standards for the maximum allowable concentration of THMs in drinking water. In other countries such as the United States of America, the United States Environmental Protection Agency (USEPA) has mandated a regular check for THMs of public water systems and had initially set a maximum allowable maximum limit of 100 µg/L for total THMs (TTHMs), later reducing this limit to 80 µg/L based on the possibility that there was an increased risk of bladder and colorectal cancer over a lifetime of drinking water with THMs above the 80 µg/L concentration (USEPA, ICR, 17 August 2011). Similarly, the Canadian and the Romanian drinking water guidelines for TTHMs are set at 100 µg/L (Ristoiu *et al.,* 2009).

The acceptable drinking water quality in South Africa is governed by the SABS, which issues drinking water standards for the different parameters as listed in SANS 241 (2005). The recommended operational limit for TTHMs is <200 µg/L and the maximum allowable limit for TTHMs is between 200 to 300 µg/L for a maximum period of 10 years. The latest issue of SANS 241 (2011) and the WHO report (2011) lists the same guideline values for THMs and TTHMs (Table 3-1). The WHO report (2011) states that THM concentrations in treated or chlorinated water should generally be below 100 µg/L. However, the TTHM concentration measured so far in South African chlorinated water varied from 200 to 1250 µg/L, in certain instances (Nothnagel *et al.,* 2008), far exceeding the maximum allowable limit listed in the SANS guidelines. It is for this reason that the monitoring of TTHMs should be implemented as a precautionary measure in all DWTPs as a means of controlling their presence prior to distribution of water into communities.

Table 3-1: Comparison of the different Trihalomethanes criteria in drinking water

Country/Standard	Organic contaminant	Criteria (µg/L)	Reference
Standards			
South Africa (SANS 241:2005)	Total THMs	200 - 300	SANS 241 (2005)
South Africa (SANS 241:2011)	Chloroform	≤300	SANS 241 (2011)
	Bromoform	≤100	
	Dibromochloromethane	≤100	
	Bromodichloromethane	≤60	
USA (EPA)	Total THMs	80	EPA (2001)
Guidelines			
Canadian	Total THMs	100	EPA (2001)
Romanian	Total THMs	100	EPA (2001)
Europe	Total THMs	100	European Drinking Water Directive 98/83/EC (1998)
WHO	Chloroform	300	WHO Guidelines for Drinking-water Quality 4th Edition (2011)
	Bromoform	100	
	Dibromochloromethane	100	
	Bromodichloromethane	60	

Table 3-1 confirms that chloroform is one of the most prevalent THMs in chlorinated water systems. While it is listed by the USEPA as a possible carcinogen, it has been given the maximum limit of 300 µg/L in SANS (2011) and WHO (2011) guidelines when compared to other THMs. As indicated by Nothnagel *et al.* (2008), the maximum THM concentration measured in five provinces of South Africa (namely Free State, Gauteng, Kwazulu-Natal, North West and Northern Cape) exceeded the maximum SANS limit (maximum measured values were ~1250 µg/L). This means that strict control measures need to be taken regarding the concentration of THMs in treated water even if it means removing as much THM precursors (such as NOM) as possible from the raw water.

3.1.1.2 Acceptable limits for perfluorocarbons in drinking water

The acceptable drinking water quality is governed by the SABS, which issues drinking water standards for the different parameters as found in SANS 241: 2005. Microbial, physical, organoleptic and chemical safety requirements are all specified in the standards with no mention of any of the perfluorinated compounds (PFCs). The standard was revised in 2011 (i.e. SANS 241:2011) without incorporating PFCs as parameters of concern. Similarly, the latest WHO report (2011) also does not contain PFCs guidelines, although several research reports alluded to their presence in drinking water systems. However, based on the results obtained from various PFC contamination studies worldwide, several countries have found it necessary to develop health-based values as guidelines for acceptable PFC levels and maximum allowable concentrations in drinking water for human consumption. This is based on detrimental human health effects, as there is no existing national legislation that defines specific limit values for all PFCs. Since there is a dearth of information on guidelines for other PFCs in comparison to those listed for PFOA and PFOS, this section focused on limited and published drinking water guidelines and information from different countries to support the research objectives concerning the drinking water guidelines for PFCs.

The following is a summary of a few guidelines issued in various countries:

(i) In 2009, the USEPA Office of Water Affairs issued drinking water Provisional Health Advisories for PFOA and PFOS of 400 ng/L and 200 ng/L, respectively (USEPA, 2009). Furthermore, in the United States of America (USA) where contamination around production plants has been identified, a site-specific action level of 500 ng/L has been set as an upper safer limit for PFOA in drinking water. The New Jersey Department of Environmental Protection has recommended a preliminary health-based guidance value of 40 ng/L for PFOA in drinking water, which is a precautionary

upper limit requiring continuous monitoring more than an action-orientated limit requiring the reduction of the contaminants in the water (Rumsby *et al.*, 2009).

(ii) In 2006, the Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency performed assessments to determine the maximum tolerable concentration of PFCs in drinking water. A Health-based Precautionary Value (HPV) of 100 ng/L was issued for both PFOA and PFOS, as these PFCs are classified as substances that are unlikely to be genotoxic, i.e. non- or low-potency genotoxic substances. For highly genotoxic substances, a maximum allowable value of 10 ng/L is deemed acceptable. While neither PFOA nor PFOS has been proven to have direct genotoxic effects, further studies are required for PFOA and PFOS. Until such clinical assessments have occurred, a HPV of 100 ng/L is used as a guideline limit for PFOA and PFOS. This value applies to lifelong exposure limitations (The Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency, 2006).

(iii) In addition, Precautionary Action Values (PAVs) for PFOA and PFOS can also be used as guidelines for remedial action for public DWTP, as summarised in Table 3-2 (The Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency, 2006):

Table 3-2: Precautionary action values for composite PFOA and PFOS levels issued by the German Drinking Water Commission, 2006

Acronym	Guidance value (ng/L)	Tolerance
PAV_{10}	>100 – 600	Tolerable for a maximum of 10 years
PAV_3	>600 – 1500	Tolerable for a maximum of 3 years
PAV_1	>1500 – 5000	Tolerable for a maximum of 1 year
PAV_0	5000	Requires immediate action to reduce adults' intake of PFOA and PFOS in drinking water

These PAVs are practical health-orientated values that take into account the lack of data as well as the possibility that some toxic risks attributable to additional perfluorocarbons with shorter or longer chains than PFOA and PFOS have yet to be identified. Consequently, these PAVs are lower than is justified from a strictly toxicological standpoint.

On the other hand, the guidance values (PAVs) were modified for infants and expectant women. For instance, infants need five to ten times more fluids per day and per kilogram of body mass compared to adults and older children. If the PAV_0 value of 5000 ng/L is reduced by the maximum factor of 10, this results in a PAV of 500 ng/L for infants, which also applies to pregnant women since PFOA and PFOS can pass through the placenta,

quantified as prevalent in cord blood. According to the Drinking Water Commission of Germany, this means that drinking water containing a composite of PFOA and PFOS concentration exceeding 500 ng/L should not be used for infant food (The Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency, 2006).

Table 3-3 summarises the maximum guidance values for PFOA and PFOS concentrations in drinking water as presented in the report (The Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency, 2006).

Table 3-3: Summary of maximum guidance values for composite PFOA and PFOS concentrations in drinking water, issued by the Drinking Water Commission, 2006

Type of maximum value	Guidance value (ng/L)
HPV for non-genotoxic substances	100
PAV for safe lifelong exposure of all population groups	300
PAV for infants and pregnant women	500
PAV_0 for adults	5000

(iii) In 2007, the United Kingdom Drinking Water Inspectorate of England and Wales issued guidelines for PFOA and PFOS using a three level-tiered system with values ranging from 300 to 9000 ng/L, with requirements for increased monitoring to decrease PFC concentration (Table 3-4).

Table 3-4: Drinking Water Inspectorate Guidance Levels for PFOS and PFOA (Rumsby, *et al.,* 2009)

Acronym	Guidance value (ng/L)
PFOS	
Tier 1	>300
Tier 2	>1000
Tier 3	>9000
PFOA	
Tier 1	>300
Tier 2	>10000
Tier 3	>90000

Minimum actions to be taken in each of these cases is as follows:

Tier 1: Local health professionals to be consulted and monitoring of PFOA and PFOS levels in drinking water is to continue.

Tier 2: Action to be taken as in Tier 1, measures to be put in place to reduce concentrations to below 1000 ng/L for PFOS or 10000 ng/L for PFOA as soon as practical.

Tier 3: Action to be taken as in Tier 2, local health professionals to be consulted as soon as possible and exposure from drinking water to be reduced within seven days (Rumsby *et al.*, 2009).

Table 3-5 list comparative values for PFOA and PFOS safer limits for various countries.

Table 3-5: Comparison of perfluorocarbons upper safer limit for drinking water for different countries

Country/Standard	Analyte	Limit/guideline value (ng/L)	Reference
South Africa (SANS 241:2005)	PFCs	Not listed	SANS 241 (2005)
South Africa (SANS 241:2011)	PFCs	Not listed	SANS 241 (2011)
WHO (2011)	PFCs	Not listed	WHO Guidelines for Drinking-water Quality 4th Edition (2011)
USA (EPA, 2009)	PFOA PFOS	400 200	USEPA (2009)
Germany	PFOA/PFOS	100	Drinking Water Commission report (2006) (see references)
United Kingdom	PFOA PFOS	300 - 9000 300 - 90000	Rumsby *et al.* (2009)
United States	PFOA	500	Rumsby *et al.* (2009)
New Jersey	PFOA	40	Rumsby *et al.* (2009)

Table 3-5 makes it evident that various countries employ different monitoring procedures with different guideline values. Safer upper limits for PFCs in drinking water systems in developing countries such as South Africa need to be listed in the National Drinking Water Standard. Unfortunately, although it is evident that PFCs exist and have detrimental effects to human health, the latest SANS 241 (2011) and the WHO (2011) report do not list any PFCs as parameters of concern. In addition, attention is currently on PFOS and PFOA only, while other lesser known PFCs have not been widely studied; consequently thus their guideline values are not listed in any of the published drinking water guidelines. This poses a serious concern.

CHAPTER 4

MATERIALS AND METHODS

CHAPTER 4
MATERIALS AND METHODS

4.1 Introduction

In this study, the method used for Trihalomethanes (THMs) analysis was liquid-liquid extraction – gas chromatography – electron capture detection method (LLE-GC-ECD) based on the EPA method 501.2 (USEPA, 1979), with minor modifications. The first step was the extraction of THMs using pentane as the extraction solvent, followed by analysis using the GC-ECD. The EPA 501.2 method was modified (detailed in sub-section 4.2.8) for the purpose of this study. Similarly, Perfluorinated compounds (PFCs) were also analysed in accordance with EPA method 537-31 (USEPA, 2009), which entails solid phase extraction (SPE), followed by analysis using LC/MS/MS method (liquid chromatography/tandem mass spectrometer). This method has been used for PFC analysis by researchers worldwide (Bao *et al.*, 2010; Wilhelm *et al.*, 2009; Post *et al.*, 2009; Orata *et al.*, 2009; Murakami *et al.*, 2009). Analysis for water quality parameters such as conductivity, total dissolved solids, salinity, dissolved oxygen, and temperature were analysed using the YSI multi-function probe. Furthermore, the concentration of phosphates was quantified using Merck cell test kits whereas NOM was measured as TOC using the Spectroquant TOC test kit. The subsequent sections describe in detail materials and methods for the quantification of THMs, PFCs and water characteristics.

4.2 Trihalomethanes (THMs)

4.2.1 Instrumentation used in Trihalomethane analysis

A number of studies have compared different methods for the determination of volatile organic compounds in drinking water, including THMs. The different methods compared were the liquid-liquid extraction-gas chromatography-electron capture detection (LLE-GC-ECD), liquid-liquid extraction-gas chromatography-mass spectrometry (LLE-GC-MS), purge and trap-gas chromatography-mass spectrometry (P/T-GC-MS) and headspace-gas chromatography-mass spectrometry (HS-GC-MS). The comparisons were based on the minimum levels of detection (MLD) – see Table 4-1.

Table 4-1: Minimum levels of detection using different Gas Chromatography instruments

Method	MLD (µg/L)	Reference
LLE-GC-ECD	<0.1	Culea *et al.* (2006)
LLE-GC-MS	<0.2	Culea *et al,* (2009)
P/T-GC-MS	1	Culea *et al.* (2006)
HS-GC-MS	<0.1	Culea *et al.* (2006)

The LLE-GC-MS method was found to be simple and more rapid method than the other methods but the use of methyl tert-butyl ether (MTBE) as solvent is a disadvantage when this solvent is of interest in some water samples. Another disadvantage of the LLE-GC-MS method is the inability to concentrate the extract because of the potential loss of the volatile compounds (Culea *et al.*, 2006; Culea *et al.*, 2009). Furthermore, comparison studies have shown that electron capture detection (ECD) method is the most sensitive detector for halogenated compounds, while the purge and trap (P/T) and HS methods are limited to above the ppb (ng/L) range. These methods can be subjected to airborne or solvent contamination and often give high blank values (Trehy, 2001). The (P/T) method has been proven to be useful for volatile organic compounds (VOCs) identification in water because the sensitivity could be easily improved by using a larger water sample and a longer extraction time (Culea *et al.*, 2009) and it is applicable for the quantitative and qualitative determination of VOCs in water samples. The concentration factor obtained by trapping the analytes selectively on an adsorbent material allows analysis of samples with very low concentration (Trey, 2001). For this study, the LLE-GC-ECD method was deemed appropriate (EPA method 501.2). The same method was used by Kozani *et al.* (2007) and Karim *et al.* (2011).

4.2.2 Apparatus (modified EPA Method 501.2)

The sample bottles, extraction, and volumetric flasks used were washed with water containing detergent, rinsed with tap water and finally with de-ionised water prior to drying. The sample bottles were air dried and then placed in an oven at 105°C for one hour and then allowed to cool. Table 4-2 lists the apparatus used for water preparation and THM analysis.

Table 4-2: Apparatus used for water preparation and Trihalomethane analysis

Apparatus	Classification/Description
Extraction vessel	15 mL total volume glass vessel with glass screw cap
Sampling containers	2 L Polypropylene bottles with screw caps
Micro syringes	10, 100 μL
Glass stoppered volumetric flasks	10, 100 mL
Measuring cylinders	10, 50 mL polypropylene
Test tubes	15 mL polypropylene
Gas chromatograph with linearized ECD	Temperature programmable
Column	DB5-26, 30 m, 0.53 mm, 1.0 μm *d*f HP-1 (Agilent Technologies, USA)
Sample vials	2 mL amber screw-cap septum bottles with Teflon faced silicone septa

4.2.3 Reagents and analytical procedures for Trihalomethane analysis

All reagents used were of analytical grade standard. Furthermore, the methanol was distilled to ensure minimal interference of any impurities. Control samples (aerated distilled water) were filtered using activated carbon, while the pentane and 1,2 dibromo 3-chloropropane, were used as the extraction solvent and an internal standard, respectively (Table 4-3).

Table 4-3: Reagents used for Trihalomethane analysis

Type	Reagents/grade
Chlorine reducing agent	Sodium thiosulphate (ACS Reagent grade)
Extraction solvent	Pentane (analytical grade)
Methanol	ACS Reagent analytical grade
Activated carbon	Filtrasorb-200
Standards (analytes)	Bromoform – 96% Bromodichloromethane – 97% Chlorodibromomethane - 99% Chloroform – 99%
Internal standard	1,2 dibromo 3-chloropropane
Organic free water	Aerated water filtered through activated carbon

4.2.4 Sample collection, handling and storage

All samples were handled in the following manner:

Samples (treated water) were collected in 2 L Polypropylene bottles with screw caps. Sodium thiosulphate was added to all the samples after sample collection to prevent formation of additional THMs. Sample bottles were then filled in such a manner that no air bubbles were entrapped. Sample blanks were prepared in duplicate with organic-free water prior to shipping the sample bottles to the sampling site and were shipped along with the sample

bottles from the sampling site back to the laboratory. An identical amount of sodium thiosulphate was added to the blanks. Samples and the blanks were stored as a set in the refrigerator at ±4°C for a period of 48 hours to 1 week (maximum) prior to analysis.

4.2.5 Sampling sites, frequency, Trihalomethane extraction process and GC-ECD operational conditions

Samples were collected from the following drinking water treatment plants (DWTPs) and drinking water distribution stations (DWDS): Atlantis, Blackheath, Brooklands, Faure, Steenbras, Voelvlei, and Wemmershoek, and from the Plattekloof reservoir (inlet and outlet). Several batches (n = 4) were collected from the DWTPs to ascertain consistency in THM prevalence, with other batches (n = 2) collected from tap water in several Western Cape suburbs and townships for a period of three months (October to December 2012) – when access to the DWTPs and the DWDS was given without restrictions. All samples were collected in duplicate.

The THM extraction process was performed using the following three steps:

Step 1: Liquid-liquid extraction (LLE)

A volume of 8 mL of the extraction solvent (pentane) was measured using a pipette and decanted into a clean, glass stoppered extraction flask. Thereafter, 40 mL of treated water sample was measured using a measuring cylinder and added into the extraction flask and the mixture was shaken vigorously for 1 minute for homogenisation. The mixture was then allowed to stand for 5 minutes to allow separation of the layers; the bottom layer was decanted and extracted for the second time while the top layer (known as organic layer) was decanted into a 15 mL polypropylene tube. The procedure was repeated for all treated water samples so extraction was performed twice for each sample.

Step 2: Extract concentration

Extracts obtained were concentrated to under a gentle stream of high purity nitrogen to reduce the all the pentane mixture to 1 mL. The final extract was transferred into a properly labelled sample vial for analysis using the GC-ECD.

Step 3: GC-ECD conditions

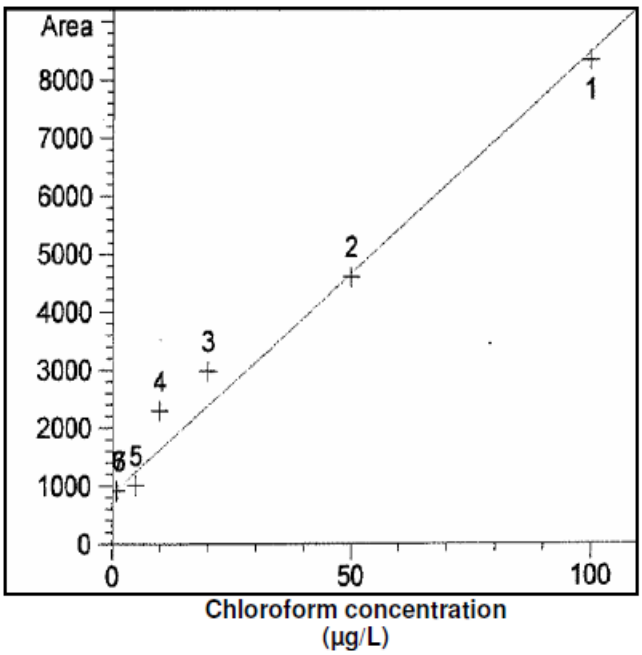
Subsequent to LLE and extract concentration, 1 μL of the extract was injected (2 injections per sample) into the gas chromatograph equipped with a linearized electron capture detector (GC-ECD) for separation and analysis. Table 4-4 lists the operational conditions of the GC-ECD.

Table 4-4: Operating parameters for the GC-ECD

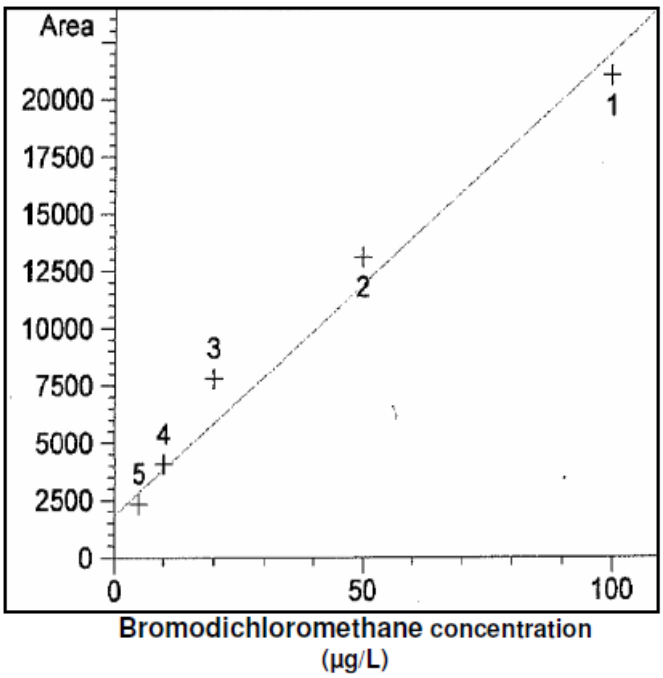
Type	Operating parameter
Column	DB5-26, 30 m, 0.53 mm, 1.0 μm *d*f (Agilent Technologies, USA)
Carrier gas	Helium at a constant inlet pressure of 15 kPa
Make-up gas	99.9% Nitrogen at 60 L/min
Injector temperature	40°C
Oven temperature	270°C
Detector temperature	300°C

4.2.6 GC-ECD calibration curves for Trihalomethanes

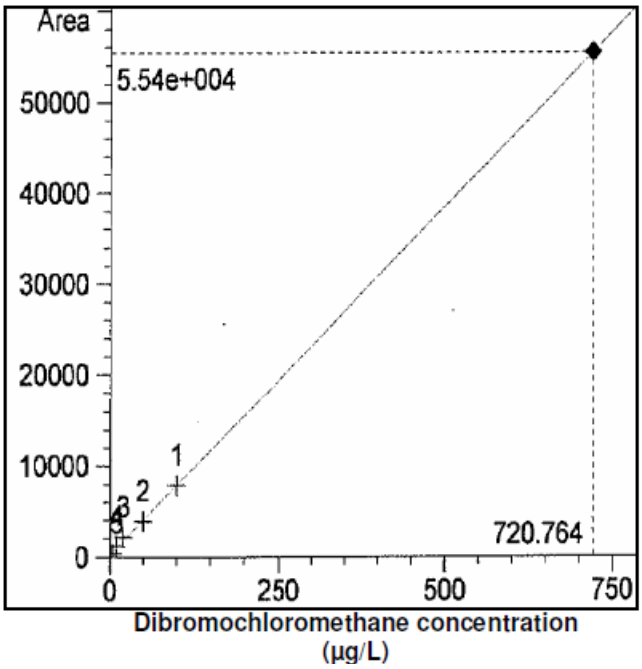
For calibration, the following standards were used: 0.1, 1.0, 5.0, 10, 20, 50 and 100 ug/L for Chloroform, Dibromochloromethane (DBCM), Bromodichloromethane (BDCM) and Bromoform. Figure 4-1 illustrates calibration curves for Chloroform (R^2 = 0.98), BDCM (R^2 = 0.98), DBCM (R^2 = 0.996) and bromoform (R^2 = 0.96) from the GC-ECD. The THMs were identified by their retention times.



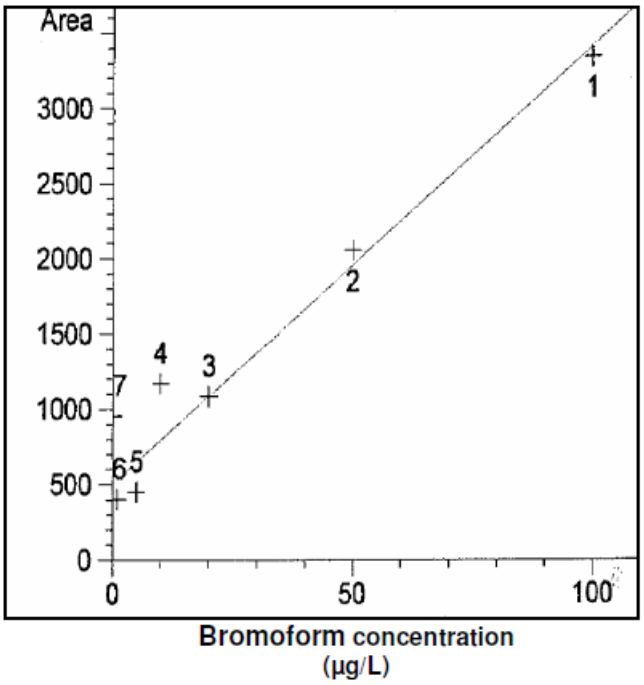
(a)



(b)



(c)

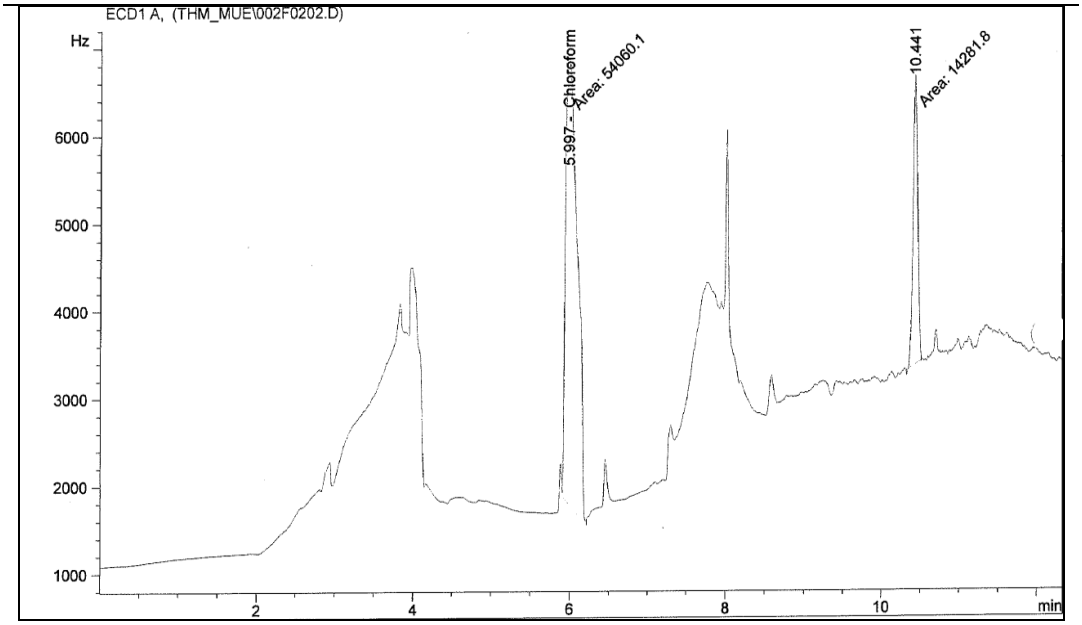


(d)

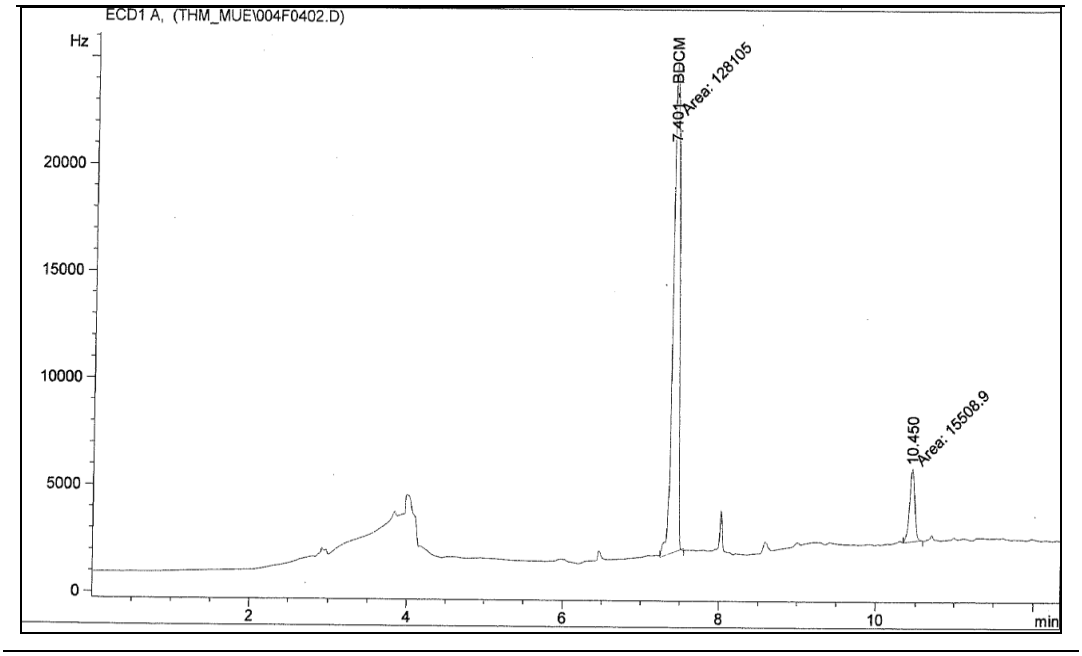
Figure 4-1: (a): Chloroform calibration curve; (b): BDCM calibration curve; (c) DBCM calibration curve; (d) Bromoform calibration curve

4.2.7 GC-ECD chromatograms for Trihalomethanes

Figure 4-2 illustrates chromatograms for Chloroform, BDCM, DBCM and Bromoform from the GC-ECD.

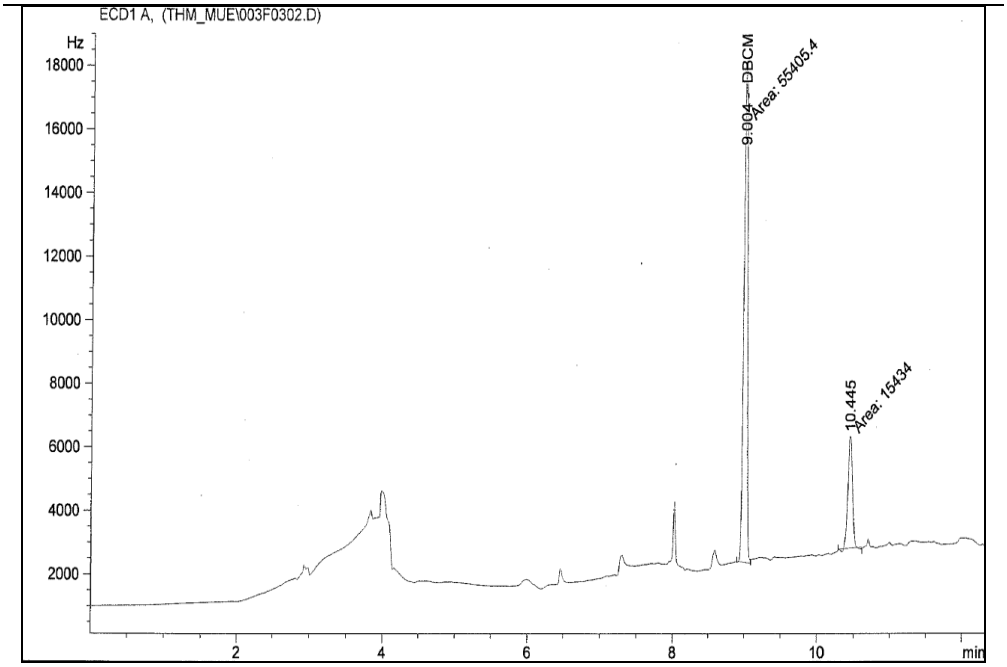


(a)

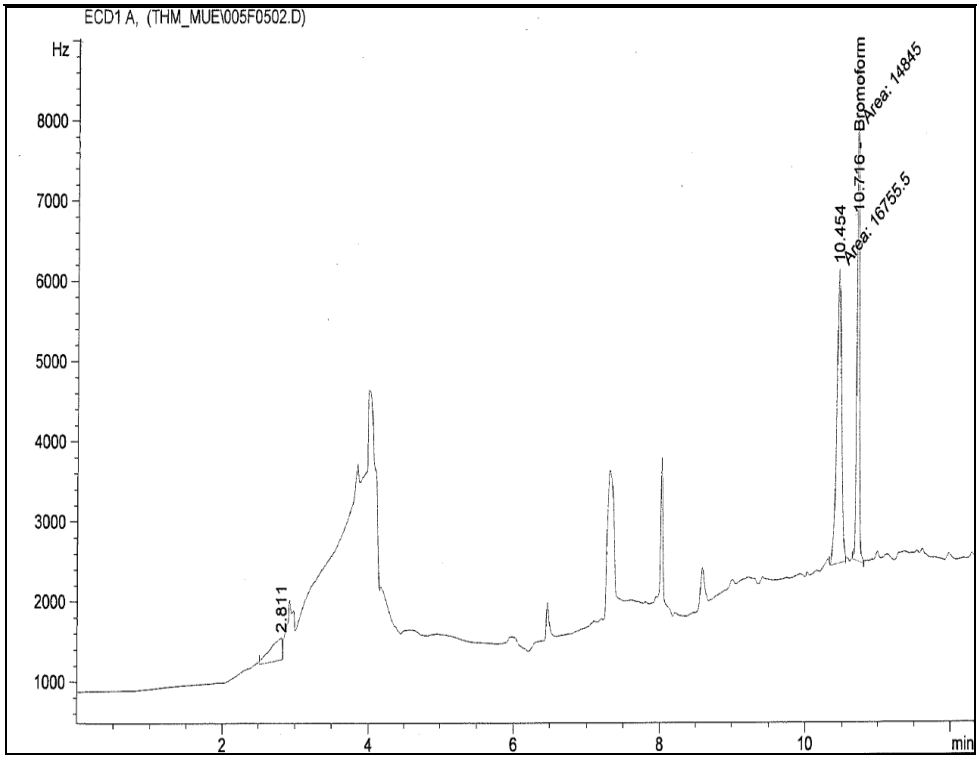


(b)

Figure 4-2: (a) Chloroform chromatogram; (b) BDCM chromatogram



(c)



(d)

Figure 4-2: *cont.* (c): DBCM chromatogram; (d): Bromoform chromatogram.

4.2.8 Method modification, validation and quality control for Trihalomethanes analysis

The volume of the sample and the extraction solvent (pentane) were changed from 10 mL (sample) and 2 mL (pentane) as used in EPA method 501.2 to 40 mL (sample) and 8 mL (solvent), respectively. These volumes were increased, as pentane is highly volatile, to improve the extraction process and minimise pentane volatilisation. Each extraction cycle was duplicated to ascertain the concentration and consistency in the extraction process for THMs for each sample.

The quality control method used in this study was developed by Rome and McIntyre (2012) and it uses relative response factors (RRF). This is explained by stating that the absolute responses of the analytes in the GC change daily and from instrument to instrument. This method is widely accepted that responses are corrected with an internal standard as the resulting RRF generally remains constant and is not affected by the changes in time of analysis or instrument. Therefore, the use of a pre-determined RRF between two analytes was used to quantify the unknown concentration of each analyte in the sample in the presence of the known concentration of the same analyte in the internal standard. The internal standard method involves the comparison of the instrument response using a known concentration of the standard, in comparison to the response of target compounds in the sample. When using the internal standard method, a known concentration of the internal standard was added to the standards of the analytes and the extraction just before analysis. The response of the target compounds was normalized to the response of the internal standard because it was contained within the aliquot of the sample extract containing analytes injected into the instrumentation.

A known concentration of the internal standard was added to all sample extracts and it was also included in each of the calibration standards. The response factor (RF) for each analyte was calculated by using the peak area and concentration of the analyte, as in Eq. 4.1:

$$RF = \frac{\text{Peak area}}{\text{Concentration}} \tag{4.1}$$

The response factors calculated for each analyte were then used to calculate the RRF between the two analytes, as in Eq. 4.2:

$$RRF = \frac{\text{RF of A}}{\text{RF of B}} \tag{4.2}$$

Where: RF of A → response factor of the analyte in the sample extract, RF of B → response factor of the analyte in the internal standard.

The RRF was then used to calculate the unknown concentration of each analyte (of the THMs in the sample) for each sample in the presence of a known concentration of analyte B (internal standard), as in Eq. 4.3:

$$\text{Concentration of A} = \frac{\text{Peak area of A}}{\text{Peak area of B}} \text{ x } \frac{1}{\text{RRF}} \text{ x Concentration of B} \qquad (4.3)$$

Where:

A → analyte in each sample,

B → analyte in the calibration standard.

Therefore, Eq. 4.3 relates the concentration of the compound to its peak area. For this study this equation was used to find the concentration of the THMs in drinking water (Rome & McIntyre, 2012).

4.3 Perfluorinated compounds (PFCs)

4.3.1 Analytical instruments used in perfluorinated compound analysis

A number of studies have compared different methods for the determination of perfluorinated compounds in various water types (Table 4-5). The primary method used is solid phase extraction (SPE) using a suitable cartridge (HLB/C_{18}) followed by analysis using LC-ESI-MS/MS for which various elution solvents are used (methanol/NH_4Ac/ethyl acetate or their combination).

Table 4-5: Extraction and instrumental analysis techniques for different water samples for perfluorinated compounds (PFOA/PFOS)

Analyte	Sample type	Pre-treatment	Extraction	SPE elution solvent	Instrumental analysis	Sample intake (LOD) [mL/(ng/L)]	Reference
PFOS/PFOA	Seawater	Filtration	SPE: Oasis HLB and C_{18}	Methanol	LC-ESI-MS/MS	1000/(0.4-5.2 pg/L)	Yamashita *et al.* (2004)
PFOS/PFOA	Water	Filtration	SPE: Oasis HLB and Oasis WAX	0.1% NH_4OH/methanol	LC-ESI-MS/MS	100-200/(0.004-4)	Taniyasu *et al.* (2005)
PFOS/PFOA	Municipal wastewater	Centrifugation	On-line SPE: C_{18}	Methanol/water/NH_4Ac	LC-ESI-MS/MS	0.5/0.5	Schultz *et al.* (2006)
PFOS	Surface water	Filtration	SPE: C_{18}	Ammonium acetate	LC-ESI/MS	0.04 - 0.1 (LOD)	Saito *et al.* (2003/2004)
PFOA	Wastewater	None	SPE (Water Oasis HLB, 1g)	Methanol	LC-ESI-MS/MS	0.06 - 0.1 (LOD)	Boulanger *et al.* (2005)
PFOS	River water	None	SPE (Oasis WAX)	Methanol	LC-ESI-MS/MS	0.01 - 1 (LOD)	Hansen *et al.* (2002)
PFOS/PFOA	Water	None	SPE: C_{18} (end-capped cartridges)	MeOH-ethyl acetate	LC-ESI-MS/MS	0.2 - 0.47 (LOD)	Gonzalez-Barreiro *et al.* (2006)

For the purpose of this study, the PFC analysis was performed on both raw and treated water and the materials including methods used for the PFC analysis are discussed in subsequent sections. The minor modification was made to the method, in particular, the water sample volume used for the extraction process, which was increased from 250 mL to 500 mL. To ensure negligible sample contamination and integrity, polypropylene sampling bottles, syringes and filters were used. Additionally, materials made of glass, ceramics or Teflon, were avoided.

4.3.2 Apparatus, reagents and sampling procedures

The sample bottles, extraction flasks, and volumetric flasks including ancillary materials were rinsed with analytical grade methanol, which was passed through a Hydrophilic-lipophilic balance (HLB) cartridge to remove any traces of PFCs. After the rinse, materials were air dried and then placed in an oven at 105°C for 1 hour and then allowed to cool. Table 4-6 lists the apparatus including reagents used for PFC analysis.

Table 4-6: Apparatus used for water sampling and perfluorinated compound analysis

Apparatus	**Classification**
Sampling containers	2 L Polypropylene bottles with screw cap
Pipette	1 mL
Measuring cylinder	10, 250 mL
Polypropylene beakers	500 mL
Collection polypropylene tubes	15 mL
Cartridges	Supel-Select HLB SPE cartridges (500 mg solid phase, 12 mL tubes)
Foil	
Vacuum pump	
Reagents	**Type/Grade**
Methanol	ACS Reagent grade
Activated carbon	Filtrasorb-200
Organic free water (Milli-Q)	Water filtered through activated carbon and HLB cartridges

4.3.3 Sample collection, handling and storage

Samples (raw and treated water) were collected in 2 L Polypropylene bottles with screw caps. Sample bottles were then filled in such a manner that no air bubbles were entrapped. Sample blanks were prepared in duplicate with organic-free water prior to shipping the sample bottles to the sampling sites and were shipped along with the sample bottles from the sampling site back to the laboratory. Samples and the blanks were stored as a set in the refrigerator at ±4°C for a period of 48 hours to 1 week (maximum) prior to analysis.

4.3.4 Sampling sites and sampling frequency

Samples were collected from the following drinking water treatment plants (DWTPs) and drinking water distribution stations (DWDS): Atlantis, Blackheath, Brooklands, Faure, Steenbras, Voelvlei, and Wemmershoek, and from the Plattekloof reservoir (inlet and outlet). Several batches (n = 4) were collected from the DWTPs to ascertain consistency in PFC prevalence for a period of three months (October to December 2012) – when access to the DWTPs and the DWDS was given without restrictions. All samples were collected in duplicate.

4.3.5 Perfluorinated compounds extraction and analysis

PFCs were analysed in accordance with modified EPA method 537-31, which entails solid phase extraction (SPE), followed by analysis using LC/MS/MS method (liquid chromatography/tandem-mass spectrometer) using five steps:

Step 1: Cartridge clean-up and conditioning

Each cartridge was rinsed with 15 mL of methanol followed by 18 mL of Milli-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 also to avoid cracking of the packing material. At this stage, it was important to ensure that the packing material did not go dry at any of the conditioning steps. If the cartridge did go dry during the conditioning phase, the conditioning was redone.

Step 2: Sample extraction

The sample extraction was done according to a modified EPA method 537-31:
About 500 mL each of spiked Milli-Q water and collected water (source and treated) samples were transferred into methanol rinsed 1L polypropylene beakers. During extraction, the vacuum was adjusted so that the approximate flow rate ranged between 8.93 to 12.5 mL/min. It was important to ensure that the cartridge did not go dry before the entire sample has passed through the cartridge during the extraction. After the 500 mL sample had passed through the cartridge, the beaker was rinsed with 10 mL of Milli-Q water and the resultant residual water was transferred into the cartridge. Thereafter, air was drawn through the cartridges for 10 minutes at high vacuum (10 to 15 in Hg) to ensure that the entire sample has been removed from the cartridge. This process was repeated for each of the duplicate samples.

Step 3: Cartridge elution

At this stage the vacuum pump was turned off to release the vacuum. The Visiprep manifold was lifted up and a thoroughly cleaned collection of polypropylene tubes were inserted into the rack to collect the extracts as they elute from the cartridges as shown in Figure 4-3.

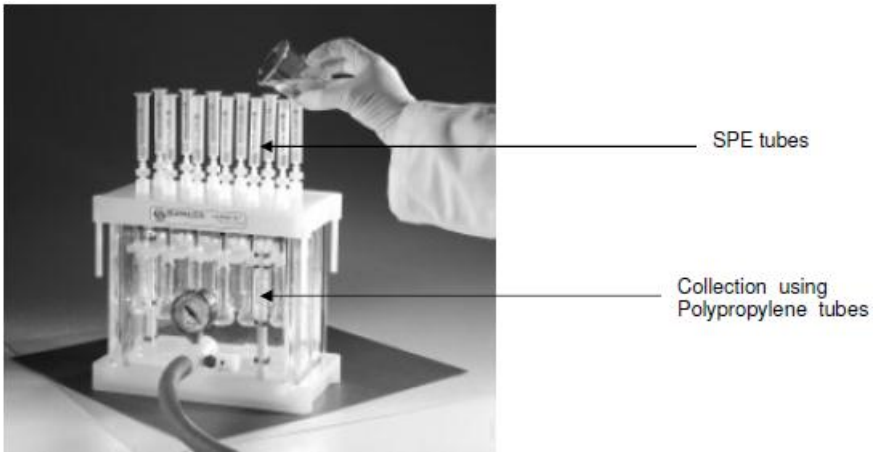


Figure 4-3: Visiprep vacuum manifold with standard lid, SPE tubes, and polypropylene collection tubes (courtesy of *Supelco, Sigma-Aldrich Co., Bulletin 910, 1998*)

Subsequently, 8 mL of methanol was transferred into individual cartridges to effect the elution of the target analytes from the cartridge. The elution was done at very low vacuum such that the solvent was leaving the cartridge in a drop-wise manner.

Step 4: Extract concentration

Extracts obtained were concentrated to ~1 mL under a gentle stream of high purity nitrogen (sometimes in a heated water bath at 60 to 65^{o}C) to reduce the methanol mixture. The final extract was then transferred into a properly labelled sample vial and stored in the refrigerator until analysis (LC/MS/MS).

Step 5: Sample analysis and calibration chromatographs

The PFC analysis was performed using the LC/MS/MS. Operating parameters are shown in Table 4-7 while Figure 4-4 illustrates the chromatographs for the seven PFCs detected with their retention times. The mean of two injected samples was used for all the samples.

Table 4-7: Summary of LC/MS/MS operational parameters used

Operational parameters	Description
1. SPE cartridge elution conditions, injection volume and final extracts volume	Elution from SPE cartridge procedure employed in this study was in accordance with that described in **USEPA Method 537-31**, although with some modifications. The details of this procedure are provided under step 3 above.
2. LC/MS/MS model used and supplier	**HPLC Model:** Ultimate 3000 Dionex HPLC system **HPLC Supplier:** Dionex Softron, Germering, Germany **MS model:** Amazon SL Ion Trap **MS supplier:** Bruker Daltonik GmbH, Bremen, Germany
3. MS/MS operational conditions and Ion mode	**MS Interface**: ESI **Dry Temp**: 350°C **Nebulizing pressure**: 60psi **Dry Gas Flow**: 10L/min **Ionisation mode**: negative **Capillary voltage**: +4500V **End plate offset**: -500V MS/MS using auto MS(n)
4. Guard column used, characteristics and supplier	No guard column used.
5. Separation column used, characteristics, supplier, temperature(i.e. operational parameters)	**Separation mode**: reversed phase chromatography **Column**: Waters Sunfire C18 column 5 µm; 4.6 × 150 mm **Supplier**: Waters, Dublin, Ireland **Column Temperature used**: 30°C
6. Mobile phase constituents, concentration, flow rate, and gradient operational parameters:	**Mobile phase**: Solvent B: 100% Acetonitrile; solvent C: 5mM CH_3COONH_4 **Flow Rate**: 0.8mL/min **Gradient**: T1 (0.00 min) = 3 6% Acetonitrile T2 (12.00 min) = 56% Acetonitrile T3 (13.00 min) = 99% Acetonitrile T4 (13.10 min) = 36% Acetonitrile T5 (20.00 min) = 36% Acetonitrile
7. Calibration standards used, concentration, range used, and supplier:	Calibration standards consist of the following levels, namely: 0, 0.1, 0.2, 0.5, 1.0, 2.5 and 5.0 ppm (for other PFCx), while the calibration levels for PFOA and PFOS consist of: 0, 0.2, 0.4, 1.0, 2.0, 5.0 and 10 ppm. All standards were supplied by Sigma-Aldrich.

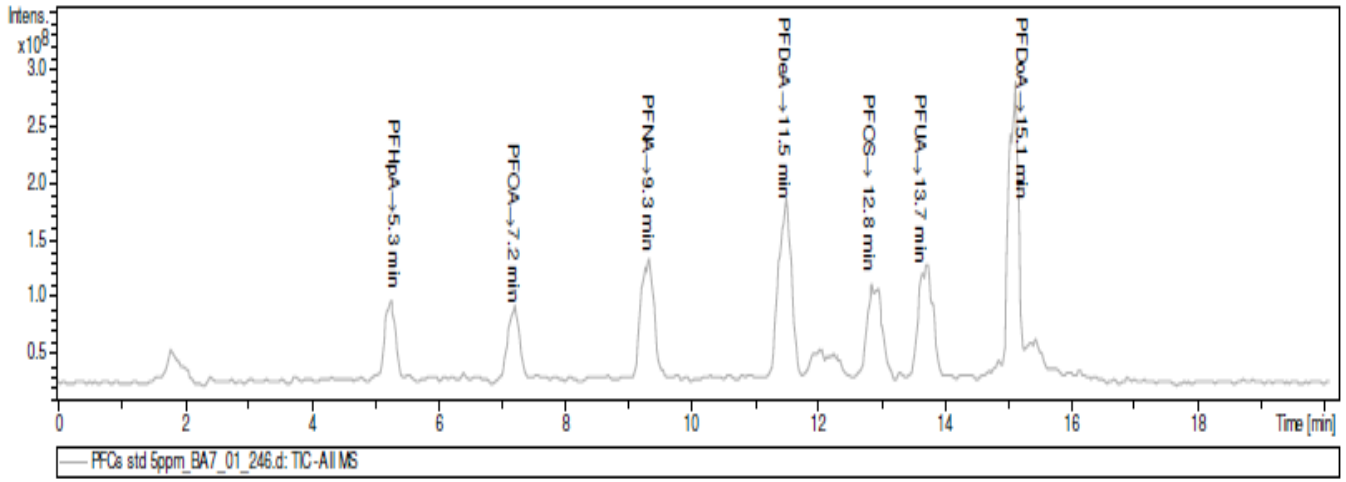


Figure 4-4: LC/MS/MS chromatograms for Perfluoroheptanoic acid (PFHpA, RT = 5.3 min, m/z 362.7), Perfluorooctanoic acid (PFOA, RT = 7.2 min, m/z 412.7), Perfluorononanoic acid (PFNA, RT = 9.3 min, m/z 462.8), Perfluorodecanoic acid (PFDeA, RT = 11.5 min, m/z 512.8), Perfluorooctane sulfonate (PFOS, RT = 12.8 min, m/z 498.8), Perfluoroundecanoic acid (PFUA, RT = 13.7 min, m/z 562.9), and Perfluorododecanoic acid (PFDoA, RT = 15.1 min, m/z 612.9

)

4.3.6 Method modification, validation and quality control for Perfluorocarbons

Water sample volume used for the extraction process was increased from 250 mL to 500 mL. Each extraction cycle was duplicated to ascertain the concentration and consistency in the extraction process for PFCs for each sample. For quality control, blank samples of Milli-Q (de-ionised water) were used with each extraction batch to confirm that potential background contaminants were not interfering with the identification or quantitation of method analytes. Analytes (PFDoA and PFUA) in the blank samples were only detected in one batch only of the three batches that were analysed for PFCs and the concentrations were negligible. Calibration standards were analysed at the beginning of each analysis batch. The final analyte concentration was determined as follows:

(i) The concentrations of the analytes detected in the blank samples were subtracted from the concentration of the respective analytes detected in the samples.

(ii) The final concentration was calculated as follows:

$$\text{Final analyte concentration} = \frac{\text{Concentration detected} \times \text{Sample volume injected}}{\text{Sample volume exctracted}} \quad (4.4)$$

4.4 Analytical Methods: Characterisation of collected water

4.4.1 Free chlorine analysis

Free chlorine analysis was performed using the Merck Spectroquant Chlorine test kit, which is USEPA approved method 330.5 drinking water (USEPA, 1978).

Table 4-8: Apparatus and reagents used for performing free chlorine analysis

Apparatus	Reagents
Autoselector	Reagent Cl_2-1
10 mL pipette	Sodium hydroxide solution 1M
20 mL rectangular cells	Sulfuric acid solution 0.5M
Neutralit indicator strips (pH 5.0 - 10.0)	-
Alicit indicator strips (pH 0 - 6.0)	-

Procedure: Free chlorine analysis

10 mL of water samples were transferred using a pipette into a 20 ml rectangular cell. The temperature and pH of the sample were within the specified ranges, i.e. 5 to 40°C and 4 - 8, respectively. One (1) level microspoon (1 sachet) of reagent Cl_2-1 was added into the rectangular cell and the mixture was shaken vigorously until the reagent was completely dissolved. The solution was left to stand for 1 minute (reaction time), and then the 20 mL rectangular cell was filled with the sample. The solution was measured using a spectrophotometer HACH DR 2800.

4.4.2 Natural organic matter analysis

Since NOM (including humic substances) is considered the most important precursor of THMs formation and has no direct method of measurement (Rizzo *et al.*, 2005), in this study NOM was measured as Total Organic Carbon (TOC) using the Spectroquant TOC test kit. This method involves the digestion with sulphuric acid (H_2SO_4) and peroxodisulphate ($S_2O_8^{2-}$ or $Na_2S_2O_8$), whereby the carbon containing compounds are transformed into carbon dioxide. This reacts with an indicator solution, the colour of which is determined photometrically. Inorganic bound carbon (dissolved carbon dioxide and anions of carbon dioxide) is expelled in gaseous form beforehand by acidification.

Table 4-9: Apparatus and reagents used for total organic carbon (NOM) analysis

Apparatus	Reagents
Reaction cells	Reagent TOC-1K
Numbering stickers	Reagent TOC-2K
5 mL pipette	-
A Thermo-reactor	-
50 mL glass beakers	-

Procedure: Natural organic matter analysis

Samples were initially digested with sulphuric acid and peroxodisulphate for the transformation of carbon-containing compounds into carbon dioxide. Thereafter, 25 mL of the samples were transferred into glass beakers and 3 drops of reagent TOC-1K were added into the digested solutions, followed by mixing and stirring for 10 minutes at medium speed. 3 mL of the stirred samples were then transferred into reaction cells to which one microspoon of reagent TOC-2K was added into each sample. The cells were then heated at 120°C in the preheated thermo-reactor for 120 minutes. After heating, the closed reaction cells were

allowed to cool to room temperature for 60 minutes in a test-tube rack. Subsequently, TOC as NOM was quantified using Spectroquant NOVA 60.

4.4.3 Water quality parameters

The YSI Professional Plus Water Quality Instrument (Pro Plus, model number 6050000, manufactured in USA, 2009) multi-function probe was used to quantify the following parameters: pH, conductivity, dissolved oxygen, salinity and total dissolved solids (TDS).

4.4.4 Phosphate analysis

The concentration of phosphates in the water was analysed using Merck test kits with a measuring range of 0.05 to 5.00 mg/l PO_4-P (Darmstadt, Germany) and a Spectroquant NOVA 60, which is a USEPA approved method for the determination of orthophosphate and total phosphorus in drinking water (analogous to EPA method 365.2-3). This method involves the digestion of orthophosphate ions (PO_4^{3-}) in sulphuric acid, which react with molybdate ions (MoO_4^{2-}) to form molybdophosphoric acid ($H_3PMo_{12}O_{40}$). This molybdophosphoric acid is then reduced by ascorbic acid to phosphomolybdenum blue (PMB) that is determined photometrically using the Spectroquant NOVA 60.

Table 4-10: Apparatus and reagents used for phosphate analysis

Apparatus	Reagents
Reaction cells	Reagent P-1K
Numbering stickers	Reagent P-2K
5 mL pipette	Reagent P-3K
A Thermo-reactor	-

Procedure: Phosphate analysis as total phosphorus

Step 1:

5 mL of samples were transferred using a pipette into the reaction cells, to which 1 dose of reagent P-1K was added into the reaction cells followed by mixing. The reaction cells for the different water samples were then heated at 120°C in a preheated thermo-reactor for 30 minutes. After 30 minutes, the closed reaction cells were allowed to cool to room temperature in a test-tube rack.

Step 2:

5 drops of reagent P-2K and 1 dose of reagent P-3K were added into the cool reaction cells containing the samples and the mixture was shaken vigorously until the reagents were completely dissolved. The reaction cells with the solution were left to stand for 5 minutes to allow reaction time and a measurement was taken using the Spectroquant NOVA 60.

CHAPTER FIVE

RESULTS AND DISCUSSION

CHAPTER 5
RESULTS AND DISCUSSION

5.1 Concentrations of Trihalomethanes in drinking water sources of the Western Cape, South Africa

The averaged concentrations of the water quality parameters and the Trihalomethanes (THMs) detected in drinking water from the seven DWTPs and a DWDS are presented in Table 5-1. The water quality parameters that have been shown to have an effect on THM formation are pH, water temperature, TOC, chlorine dosage and free chlorine (Ristoiu *et al.*, 2009; Yamada *et al.*, 1998, and Chowdhury & Champagne, 2008), and the current study focused on their effect on THM formation:

pH values increased after chlorination for all the water treatment plants. This change in pH values post chlorination was consistent with the changes observed by Ye *et al.* (2009) for the study that was performed in drinking water sources from six cities in China, whereas most researchers did not measure pH values post chlorination. Furthermore, Faure had the lowest raw water pH but the treated water pH was comparable with the other pH values determined for other treatment plants.

TOC values for raw water were highest for Faure (7.45 mg/L) followed by Steenbras (6.78 mg/L), and the lowest concentration of TOC was detected for Wemmershoek (2.26 mg/L) and Atlantis (2.45 mg/L). However, for the treated water, the majority of the TOC concentrations were below 1 mg/L and only Brooklands had a TOC concentration of 1.20 mg/L post chlorination. Overall, there was a distinguishable reduction in TOC concentration when raw water was compared to treated water. This suggests that the pre-treatment methods used in the various DWTPs were efficient in removing most of the raw water impurities.

The residual free chlorine in treated water ranged from 0.22 to 1.06 mg/L with the exception of water from the Atlantis DWTP, which had the lowest average free chlorine concentration of 0.06 mg/L. From the results shown in Table 5-1, the reduction in chlorine concentration from the concentration of chlorine dosed to the residual free chlorine was more than 50%. The cause of this accelerated chlorine decay may be due to the reaction of available chlorine with natural organic matter to form disinfection by-products such as trihalomethanes. Chlorine/NOM reactions may proceed over a period of days and environmental conditions such as pH and temperature can affect rates and the extent of by-product-forming reactions. This means that if the temperature of the water is high, chlorine decay rate will be faster as chlorine in warm water will undergo chemical reactions at a faster rate. In addition, because of chemical and hydraulic dynamics, the chemical composition of

water can vary substantially in time in distribution systems (McClellan *et al., accessed 15-11-2013*). One way that may prevent having very low residual free chlorine concentrations is by modelling chlorine decay. However, modelling chlorine decay is difficult because of the fast initial reaction with inorganic components and NOM. Therefore, the rate of chlorine decay is chlorine concentration (initial and residual) dependent (Gang *et al.,* 2003).

The averaged TTHM concentrations were in the low range and quite comparable for the seven sampling sites, ranging from low (26.52 µg/L for Plattekloof) to high (32.82 µg/L for Brooklands). The only DWTP, which had TTHM values exceeding this range, was the Atlantis DWTP, which had an average TTHM concentration of 83.48 µg/L. By comparing the individual THM concentrations, chloroform was the dominant of the four THM species in all the DWTPs, with average chloroform concentrations ranging from 11.74 µg/L for Plattekloof to 46.06 µg/L for Atlantis. Dibromochloromethane (DBCM) was the least detected of the THM species, with average concentrations ranging from 1.00 µg/L for Voelvlei to 4.94 µg/L for Atlantis. Overall, Atlantis had the highest THM concentrations for all the four THM species quantified compared to the other sampling sites (as seen in Table 5-1 and Figure 5-1). These high THM concentrations for Atlantis may be attributed to the raw water characteristics compared to other DWTPs, which means that more chlorine reacted with NOM to produce a high concentration of THMs, particularly chloroform. This can also be explained by the huge drop in the chlorine dosed and the very low concentrations of residual free chlorine in the Atlantis drinking water.

Table 5-1: Average concentrations for drinking water quality parameters and THMs detected from the selected drinking water treatment plants of the Western Cape

RAW WATER								
Parameter	**Atlantis**	**Blackheath**	**Brooklands**	**Faure**	**Plattekloof (inlet)**	**Voelvlei**	**Wemmershoek**	**Steenbras**
pH	7.10	5.18	6.00	4.56	7.04	5.69	5.62	5.83
Temp (°C)	14.03	15.88	16.20	14.47	18.00	15.95	14.03	17.50
Conductivity (µS/cm)	857	111	300	218	187	130	99	145
TDS (mg/L)	622.75	152.51	250.48	161.45	139.95	97.26	76.71	109.42
Phosphate (mg/L)	1.47	0.75	0.75	0.56	0.26	1.65	1.01	0.79
TOC raw water (mg/L)	3.42	2.45	5.77	7.45	3.98	3.65	2.26	6.78
TREATED WATER								
Parameter	**Atlantis**	**Blackheath**	**Brooklands**	**Faure**	**Plattekloof (outlet)**	**Voelvlei**	**Wemmershoek**	**Steenbras**
pH	7.62	7.73	6.52	6.39	7.04	7.10	6.52	7.33
Temp (°C)	18.90	16.17	16.35	16.60	17.85	15.03	16.70	16.17
Conductivity (µS/cm)	259	155	444	211	178	179	121	183
TDS (mg/L)	190.45	121.98	344.35	164.65	134.20	155.60	93.93	144.08
Phosphate (mg/L)	2.65	0.64	0.70	0.75	0.49	0.69	1.95	0.33
TOC treated water(mg/L)	0.38	0.39	1.20	0.88	0.79	0.83	0.56	0.64
Chlorine dose (mg/L)	2.24	1.84	3.03	2.81	2.32	4.40	1.53	1.03
Residual free chlorine (mg/L)	0.06	0.22	0.45	0.47	0.64	1.06	0.3	0.54
Chloroform (µg/L)	46.06	16.59±9.51	22.18±3.01	19.30±7.21	11.74±3.71	22.29	16.95±8.81	19.34
Bromoform (µg/L)	10.46±7.71	4.38±2.35	4.38	5.10±2.91	5.98±2.38	4.41±0.95	5.35±2.05	4.23±1.74
BDCM (µg/L)	22.02	3.28±0.91	5.14	3.71±1.71	6.94±2.43	3.88±0.94	3.56±2.18	4.04±1.18
DBCM (µg/L)	4.94	3.50±2.18	1.11±0.79	1.42±1.13	1.87±1.48	1.00	1.28	1.60
Averaged TTHMs (µg/L)	**83.48**	**27.75**	**32.82**	**29.53**	**26.52**	**31.58**	**27.14**	**29.22**

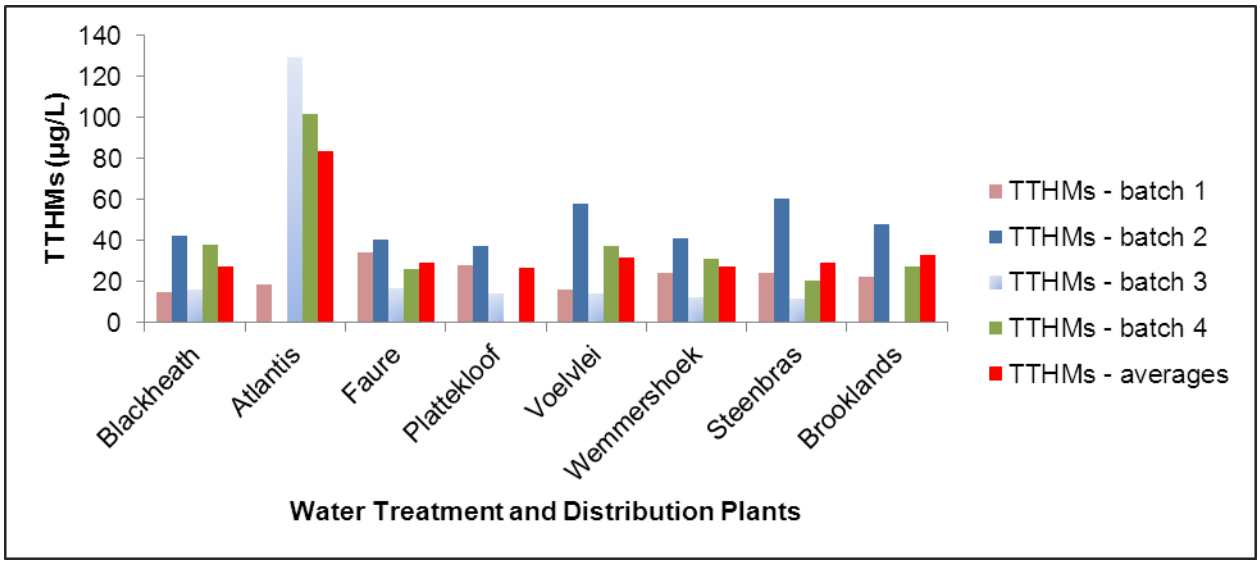


Figure 5-1: Averaged TTHM concentrations for difference water treatment and Distribution plants

5.1.1 Interpretation of results based on SANS 241:2011

The drinking water quality parameters have chemical numerical limits as listed in the SANS 241:2011. These limits are shown in Table 5-2.

Table 5-2: SANS 241:2011 aesthetic, physical, and chemical limits for drinking water

Determinand	Risk	Standard limit
Free chlorine	Chronic health	≤ 5 mg/L
Conductivity at 25°C	Aesthetic	≤ 170 000 µS/cm
Total dissolved solids	Aesthetic	≤ 1200 mg/L
pH at 25°C	Operational	5 to 9.7 pH units
TOC	Chronic health	≤ 10 mg/L

From the results obtained in this study, pH for treated water for all the drinking water treatment plants was within the SANS limits. Conductivity, total dissolved solids and free chlorine results were also very low and thus imposed no health risk for lifetime consumption of the treated water (health-related standards are based on the consumption of 2L of water per day by a person of a mass of 60 kg over a period of 70 years). Total organic carbon (TOC) detected in the treated water was below the limit of 10 mg/L, even for the raw water. The highest TOC measured as NOM was observed as 7.45 mg/L for the Faure DWTP. This was hypothesised as a contributing factor for the low THM concentrations observed post chlorination for the DWTP.

For the THMs, the SANS 241:2011 has also set limits for the individual species, which are ≤300 µg/L for chloroform, ≤100 µg/L for bromoform and DBCM, and ≤60 µg/L for BDCM (SANS 241:2011; WHO, 2011). The SANS limit for TTHMs is listed as 200 to 300 µg/L in SANS 241:2005 but it is not listed in SANS 241:2011. Although there is a need for consistent monitoring of THMs in South African drinking water, the current study indicated that TTHM concentrations, i.e. determined in the range 26.52 µg/L (Plattekloof) to 32.83 µg/L (Brooklands), were within the acceptable international limits including the SANS limits of 200 to 300 µg/L, however, the average TTHM concentration for the Atlantis DWTP exceeded the USEPA TTHM limit of 80 µg/L. Similarly, individual THM concentrations ranged from 11.74 µg/L (Plattekloof) to 46.06 µg/L (Atlantis) for chloroform; 4.23 µg/L (Steenbras) to 10.46 µg/L (Atlantis) for bromoform; 3.28 µg/L (Blackheath) to 22.02 µg/L (Atlantis) for BDCM; and lastly 1.00 µg/L (Voelvlei) to 4.94 µg/L (Atlantis) for DBCM. All these concentrations were below the SANS and WHO limits for the individual THM species.

5.1.2 Effect of different parameters on THM formation

Effect of water pH on TTHM formation

Figure 5-2 shows the correlation between pH and TTHM formation. The results obtained in this study showed minimal correlation between pH and the average TTHM formation.

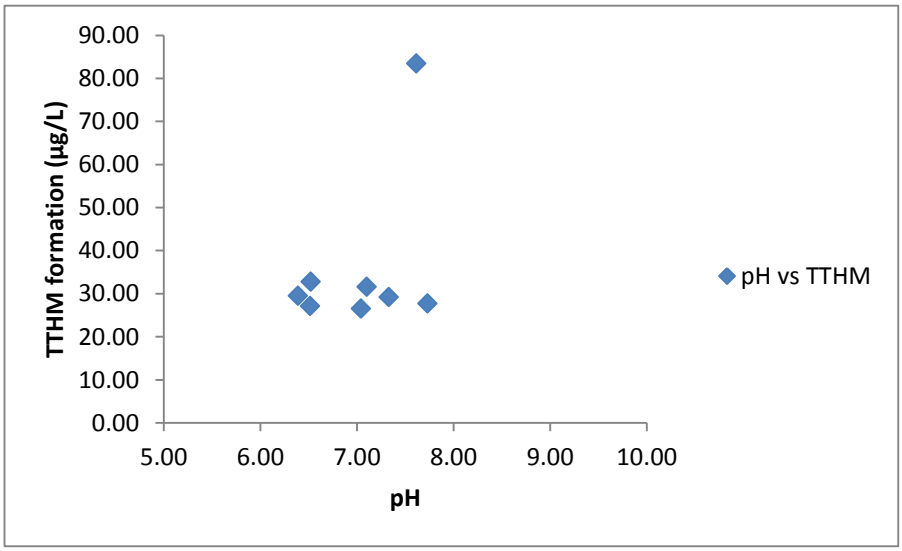


Figure 5-2: Effect of pH on TTHM formation in treated water from the various DWTP/DWDS

These results were consistent with the observations by Karim *et al.* (2011) in a study which suggested that the formation of TTHM species and distribution was largely independent of pH. In the study, the pH of all water samples was in the range of 6.7 to 8.2 (Karim *et al.*, 2011). However, in the current study, the average pH for raw water was in the range 4.56 (Faure) to 7.10 (Atlantis) with the pH of chlorinated water being in the range 6.39

to 7.73. Although the pH range of the raw water in this study was different to that of Karim *et al.* (2011), there was insignificant correlation between the observed TTHM concentrations and pH. The reason for this might be due to the fact that at higher pH values, i.e. for highly alkaline raw water, less NOM is removed whereas low pH promotes the aggregation of organic matter making it easy to remove, which can result in minimal THM formation. However, these findings contradicted with the findings of Ye *et al.* (2009) whereby observations were that there was a slight correlation between THM formation and pH, i.e. by increasing the pH from 6 to 8.5, can have a significant effect on the formation of TTHM with TTHM concentration increasing with an increase in pH (Ye *et al.*, 2009). This was further supported by results obtained by Chowdhury and Champagne (2008), whereby THM formation was found to be 40% higher when pH was changed from 6.5 to 8. In subsequent studies, Chowdhury (2013) and Hong *et al.* (2013) particularly indicated that an increase in pH resulted in an increase in chloroform concentration and a decrease in brominated DBPs, including THMs.

Effect of TOC on TTHM formation

Different compounds associated with natural organic matter (NOM) are found in raw water. This NOM reacts with chlorine to form disinfection by-products such as trihalomethanes. NOM is considered the most important precursor of THM formation but has no direct measurement. It is therefore quantified as TOC in water (Rizzo *et al.*, 2005). The results obtained in this study showing the correlation between TOC and THM/TTHM formation are shown in Tables 5-3 and 5-4. When comparing different raw water TOC concentrations with TTHM concentrations, there was insignificant deviations in the values obtained. This might be because the raw water TOC concentrations were quite low, ranging from 2.26 mg/L to 7.45 mg/L. The only outlier was Atlantis, which had a low TOC value with the highest TTHM formation. Two of the samples assessed from the Atlantis DWTP had the highest TTHM concentrations above 100 µg/L, which resulted in a TTHM average concentration of 83.48 µg/L. From the results obtained, these high concentrations were not attributed to the TOC concentrations observed; as the TOCs were comparable with those observed for the other DWTPs. Some other factors, such as chlorine dosage and the presence of other impurities in raw water, might have contributed to the high TTHM as well as the individual THM concentrations. These results were consistent with the findings by Ye *et al.* (2009), which indicated that there was a low but significant relationship between TTHM formation and TOC. A comparison between the results obtained in this study and those obtained by Ye *et al.* are shown in Table 5-4 and Figures 5-3 & 5-4.

Table 5-3: Results showing correlation between Total Organic Carbon and Trihalomethane formation

	Atlantis	Blackheath	Brooklands	Faure	Plattekloof	Voelvlei	Wemmershoek	Steenbras
TOC raw water (mg/L)	**3.42**	**2.45**	**5.77**	**7.45**	**3.98**	**3.65**	**2.26**	**6.78**
TOC treated water (mg/L)	0.38	0.39	1.20	0.88	0.79	0.83	0.56	0.64
Chlorine dose (mg/L)	2.24	1.84	3.03	2.81	2.32	4.4	1.53	1.03
Chloroform (µg/L)	46.06	16.59±9.51	22.18±3.01	19.30±7.21	11.74±3.71	22.29	16.95±8.81	19.34
Bromoform (µg/L)	10.46±7.71	4.38±2.35	4.38	5.10±2.91	5.98±2.38	4.41±0.95	5.35±2.05	4.23±1.74
BDCM (µg/L)	22.02	3.28±0.91	5.14	3.71±1.71	6.94±2.43	3.88±0.94	3.56±2.18	4.04±1.18
DBCM (µg/L)	4.94	3.50±2.18	1.11±0.79	1.42±1.13	1.87±1.48	1.00	1.28	1.60
TTHMs (µg/L)	**83.48**	**27.75**	**32.82**	**29.53**	**26.52**	**31.58**	**27.14**	**29.22**

Table 5-4: Correlations between this study and findings by Ye *et al* (2009) on the effect of Total Organic Carbon on Total THM formation

Results from this study								
	Atlantis	**Blackheath**	**Brooklands**	**Faure**	**Plattekloof**	**Voelvlei**	**Wemmershoek**	**Steenbras**
TOC raw water (mg/L)	3.42	2.45	5.77	7.45	3.98	3.65	2.26	6.78
TOC treated water(mg/L)	0.38	0.39	1.2	0.88	0.79	0.83	0.56	0.64
TTHMs (µg/L)	83.48	27.75	32.82	29.53	26.52	31.58	27.14	29.22
Findings by Ye *et al* (2009)								
	Daqing	**Beijing**	**Tianjin**	**Zhengzhou**	**Changsha**	**Shenzhen**		
TOC raw water (mg/L)	6.28	1.51	3.91	3.03	2.58	1.92		
TOC treated water(mg/L)	4.40	1.10	3.64	2.51	1.80	1.27		
TTHMs (µg/L)	13.79	10.66	42.27	35.29	10.76	11.51		

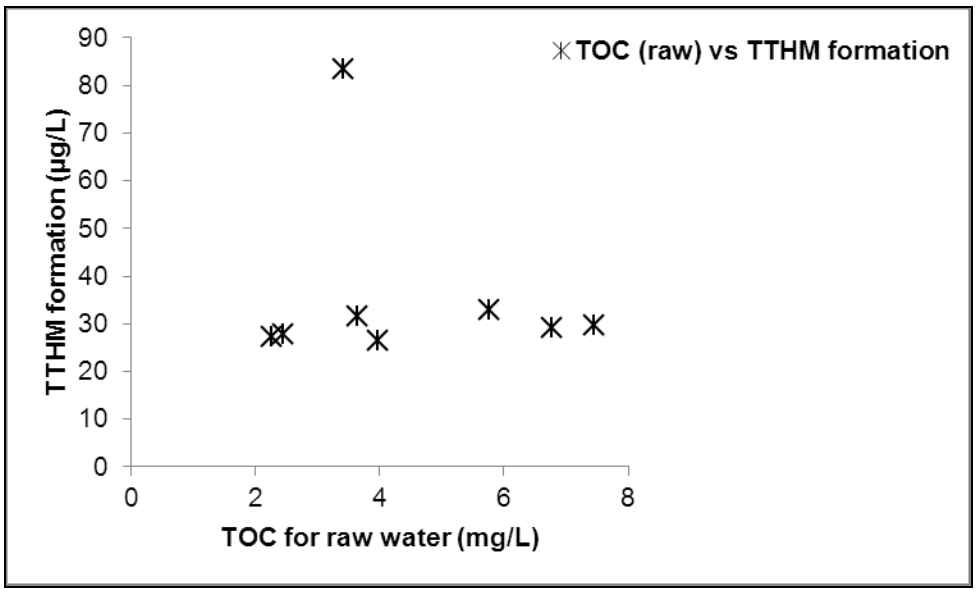


Figure 5-3: Effect of TOC on TTHM formation - results from current study,

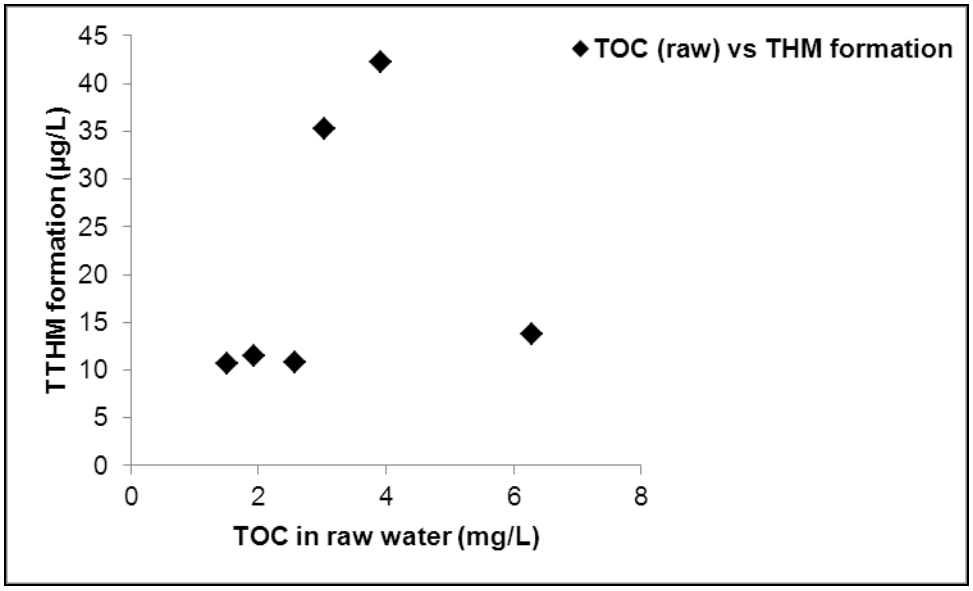


Figure 5-4: The effect of TOC on TTHM formation – findings by Ye *et al.* (2009)

In both of these studies, the TOC concentrations for raw water were low, which might be the reason why there was a limited distinct correlation. This however, does not conclude that there is no correlation between TOC and TTHM formation. These results only showed that at low TOC concentrations, there is no distinct correlation between TOC and TTHM formation. Contradiction to these findings, Ristoiu *et al.* (2009) showed that there was a direct correlation between NOM concentration and chloroform concentrations after chlorination (Ristoiu *et al.*, 2009). Similarly, Chowdhury *et al.* (2008) and Chowdhury (2013) observed that a correlation does exist between NOM and THMs formation whereby lower molecular weight NOM formed more brominated THMs than corresponding higher molecular weight NOM. Furthermore, these studies indicated that higher molecular weight NOM strongly correlated with absorbance at UV_{254}, in particular the specific ultraviolet absorbance

(SUVA), when compared to lower molecular weight NOM. Therefore, the observations from this study were consistent with some of the previous studies (Ye *et al.*, 2009) and it can be concluded that the effect of TOC concentrations on TTHM formation was not distinct at low TOC concentrations.

Effect of chlorine dose and residual chlorine on chloroform formation

Chlorine dose refers to the amount of chlorine used for disinfection (Chowdhury *et al.*, 2008). From the current study, chlorine dosed was only analysed in one batch of the samples as it is kept constant when chlorinating drinking water. The results are shown in the Table 5-5. Higher chlorine doses were proven to result in higher chloroform concentrations (Ristoiu *et al.*, 2008). From the results obtained in the current study, a trend was observed indicating that for most of the DWTPs, a higher chlorine dose resulted in a higher chloroform formation (as shown in Table 5-5 and Figure 5-6). These results were consistent with the findings of Ristoiu *et al.* (2008), Chowdhury *et al.* (2008) and Ye *et al.* (2009). Chowdhury *et al.* (2008) observed that THM concentration increased with increasing chlorine dosages but when the chlorine dosages were increased further (above 9.5 and 8.2 mg/L for Ferryland and Clarenville water samples), there was no significant increase in THM formation. This may be because beyond breakpoint, chlorine had insignificant amount of organics to react with (Chowdhury *et al.*, 2008). The breakpoint chlorination graph is shown in Figure 5-5.

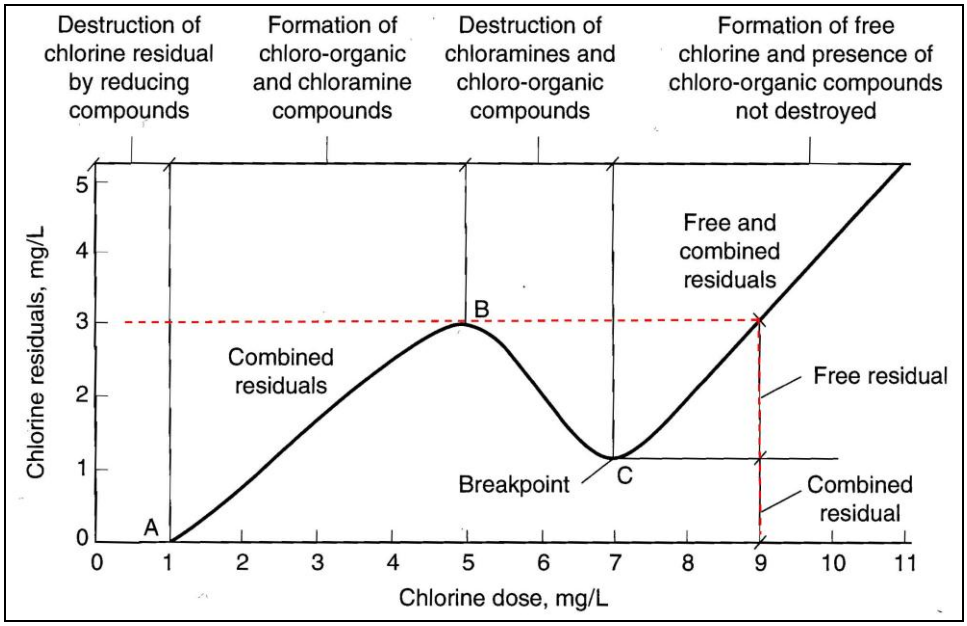


Figure 5-5: Theoretical breakpoint chlorination curve (courtesy of American Water Works Association (AWWA), 2004)

Figure 5-5 shows the amount of chlorine measured in water versus the amount of chlorine added. During breakpoint chlorination, excess chlorine in chloraminated water consumes the available ammonia, so that the remaining disinfectant residual exists as free chlorine.

When the chloramines and chloro-organic compounds are completely destroyed and converted to nitrogen gas, that is the breakpoint. Beyond the breakpoint, all chlorine added to the water remains as free chlorine (American Water Works Association (AWWA), 2004). Hence, if the total organic matter present to react with the free residual chlorine beyond breakpoint is small, THM formation will decrease.

As the residual free chlorine has an effect on the continuous formation of chloroform post-treatment, there is a high possibility of chloroform formation during distribution, as a result of the reaction between residual free chlorine with NOM in treated water. Generally, low concentrations of THMs in tap water samples may be due to low levels of residual chlorine in those samples (Karim *et al.*, 2011). Because of decomposition of DBPs, a decrease in residual chlorine can directly result in a decrease in DBP formation (Ye *et al.*, 2009). During this study, tap water samples were collected from some of the Western Cape suburbs and townships to determine primarily THM concentration and free residual chlorine. The results are presented in Table 5-6.

Table 5-5: Results showing effect of chlorine dose on chloroform formation (1 Batch)

Parameter	Atlantis	Blackheath	Brooklands	Faure	Plattekloof	Voelvlei	Wemmershoek	Steenbras
TOC raw water (mg/L)	3.42	2.45	5.77	7.45	3.98	3.65	2.26	6.78
TOC treated water (mg/L)	0.38	0.39	1.2	0.88	0.79	0.83	0.56	0.64
Residual Free chlorine (mg/L)	0.03	0.05	0.45	0.73	0.62	1.52	0.36	0.7
Chlorine dose (mg/L)	***2.24***	***1.84***	***3.03***	***2.81***	***2.32***	***4.4***	***1.53***	***1.03***
Chloroform (µg/L)	8.342	6.788	18.091	27.675	11.438	3.054	11.076	7.317
Bromoform (µg/L)	2.098	1.097	1.328	3.9	6.029	3.781	7.972	5.495
BDCM (µg/L)	3.098	2.585	1.614	2.095	8.884	5.396	1.887	4.911
DBCM (µg/L)	5.125	4.343	1.691	0.953	1.592	3.991	3.32	6.409
TTHMs	**18.663**	**14.813**	**22.724**	**34.623**	**27.943**	**16.222**	**24.255**	**24.132**

Table 5-6: Averaged residual free chlorine and THM concentrations detected from tap water samples collected from Western Cape suburbs

Parameter	Athlone	Browns Farm	Gardens	Grassy Park	Khayelitsha	Mandalay	Kraaifontein -Wallacedene
Residual Free chlorine (mg/L)	0.02	0.04	0.02	0.03	0.06	0.04	0.05
Chloroform (µg/L)	2.293	2.625	1.468	1.966	1.869	1.095	2.519
Bromoform (µg/L)	3.444	7.143	2.024	2.571	2.430	1.269	1.728
BDCM (µg/L)	3.340	3.347	5.762	3.599	2.766	2.766	3.554
DBCM (µg/L)	0.730	0.000	0.000	0.000	0.171	0.171	0.000
TTHMs (µg/L)	**9.806**	**13.115**	**9.254**	**8.137**	**7.236**	**5.301**	**7.801**
Parameter	**Mamre**	**Parklands**	**Plumstead**	**Plattekloof**	**Strandfontein**	**Summergreens**	**Kraaifontein - Northpine**
Free chlorine (mg/L)	0.04	0.02	0.03	0.02	0.05	0.04	0.04
Chloroform (µg/L)	2.095	3.051	1.970	1.939	1.548	1.723	1.201
Bromoform (µg/L)	1.216	1.108	1.153	1.458	1.616	1.963	0.830
BDCM (µg/L)	5.562	5.673	4.300	3.767	3.175	4.973	3.554
DBCM (µg/L)	0.391	0.359	0.323	0.315	0.361	0.511	0.061
TTHMs (µg/L)	**9.265**	**10.191**	**7.746**	**7.480**	**6.700**	**9.171**	**5.647**

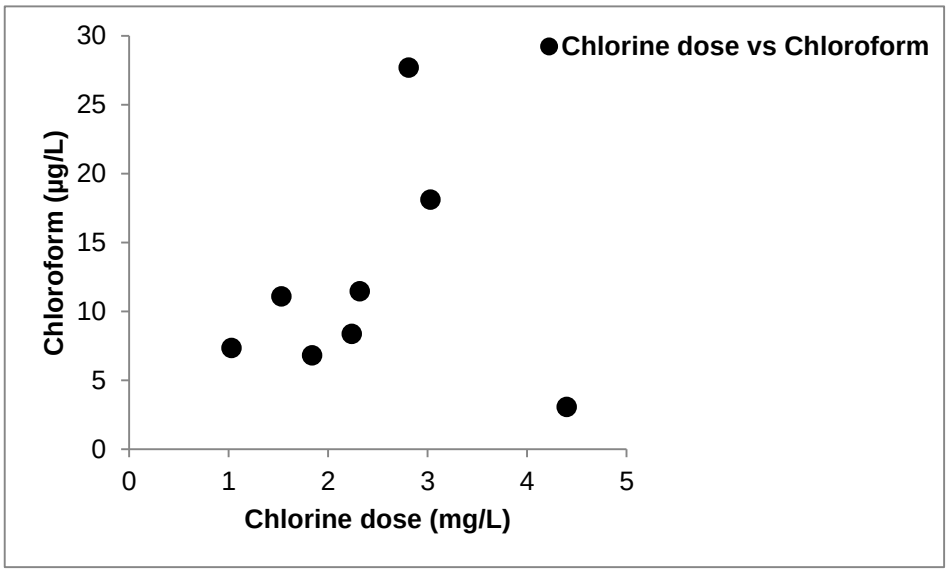


Figure 5-6: Results showing effect of chlorine dose on chloroform formation

The guideline value set by the WHO (2011) for effective disinfection is a residual free chlorine concentration of ≥ 0.5 mg/L after at least 30 minutes contact time at pH < 8.0. Residual chlorine of 0.2 to 0.3 mg/L should be maintained throughout the distribution system (WHO, 2011; Karim *et al.*, 2011). At the point of delivery, the minimum residual concentration of free chlorine should be 0.2 mg/L (WHO, 2011). From the results obtained in this study (see Table 5-5), only a single batch of the results was used to determine the effect of chlorine dose on chloroform. This is because the chlorine dose concentrations were only analysed for this batch. Although the residual free chlorine concentration after 30 minutes contact time was not determined, the average residual free chlorine concentrations in seven of the DWTP were in the range 0.03 to 1.52 mg/L, with Atlantis and Blackheath having low residual free chlorine concentrations of 0.03 mg/L and 0.05 mg/L, respectively, while Voelvlei had the highest (1.52 mg/L). A decrease in residual free chlorine is associated with the amount of organic matter present in the water, i.e. the higher the organic matter and the lower the chlorine supplied or dosed, the lower the residual free chlorine will be, and the higher the THM formation potential. From the results obtained, the average TOC concentrations for all the DWTPs and DWDS were low compared to the raw water, which means that the pre-treatment processes were effective. Hence, the TOC concentrations did not explain the low residual free chlorine concentrations obtained.

However, a decrease in residual free chlorine is expected due to the fact that chlorine decreases with time in a water-based medium as it is volatile and can react with other constituents in the water to form other by-products. This residual free chlorine can react with

water constituents such as corrosion by-products, microorganisms, organic impurities, ammonia-based compounds, etc., leading to its consumption thus minimal detection in chlorinated water. Additionally, it was determined that free chlorine is largely used up by reactions with biofilms formed on the distribution pipe walls (Karim *et al.*, 2011). Therefore, it is recommended by WHO that drinking water treatment utilities ensure that after chlorination, the initial residual free chlorine concentration is ≥ 0.5 mg/L after a contact time of at least 30 minutes at pH < 8. This is to ensure that a minimum chlorine residual of 0.2 to 0.3 mg/L is maintained throughout the distribution network. If the residual free chlorine is below this concentration, this might lead to very low or no chlorine in the farthest part of the distribution system as well as the consumer's tap, which may result in high risk of bacterial contamination of drinking water (Karim *et al.*, 2011).

Furthermore, the residual free chlorine concentrations from tap water (see Table 5-6) were also very low, ranging from 0.02 to 0.06 mg/L, for drinking water collected from various suburbs and townships in the Western Cape. Similarly, low THM concentrations (specifically chloroform) were also low in the water when compared to the THM levels quantified in water collected from DWTPs. THM concentrations largely depends on the amount of organic matter and free chlorine present in the water. Nonetheless, these results are acceptable in terms of maintaining low THMs in drinking water at the point of use; however, the overall residual free chlorine concentration observed was below that prescribed by the WHO, for which the guideline value of 0.2 mg/L at the point of delivery is recommended. On the other hand, the SANS (241:2011) only has a limit value of ≤ 5 mg/L for residual free chlorine in drinking water immediately post-chlorination, which is the maximum allowable concentration for the distribution network and point of use. The standard (SANS 241:2011) has adopted a new position for this. Emphasis is on maintaining a residual compliance that will allow adequate compliance to the microbiological parameters, which are of an acute health risk. The standard states that where a microbiological value exceeds the numerical limit set in the standard, an unacceptable risk to human health is implied, and as the microbiological value increases, an increasing risk to health is implied. However, this still does not give a clear guideline on the minimum amount of chlorine to be maintained through the distribution network and at the point of use, to ensure effective disinfection, as it is clearly explained in the WHO drinking water guidelines.

Effect of water temperature on THM formation

Some studies have shown that temperature has an effect on TTHM formation during chlorine disinfection. Ristoiu *et al.* (2008) observed that during winter, chloroform concentrations were much lower than during summer season, with a difference of almost 50%. The study further explained that this effect could be due to the slower formation of TTHM at lower temperature (temperature between 2.7 to 6.3°C in winter), together with observed lower NOM concentrations during winter. Under these conditions, chlorine demand is lower and therefore chlorine dose required to maintain adequate residual free chlorine in the distribution system is also lower (Ristoiu *et al.*, 2008). Furthermore, Chang *et al.* (2010) performed analysis on 86 water treatment plants from February to March 2007 and from July to August 2007, observing that seasonal variations had an effect on DBPs in drinking water, i.e. total THMs concentration ranged from ND to 99.4 µg/L in winter and from ND to 133.2 µg/L in summer. Furthermore, Stevens *et al.* (1976) performed experiments at three different temperatures (i.e. 3, 25 and 40°C), constant pH of 7 and chlorine dose of 10 mg/L. TTHM formation was found to be 1.5 to 2 times higher at each stage of temperature change. Hong *et al.* (2013) also observed a significant increase in THMs at elevated temperatures.

From the results obtained in the current study, the water samples were only collected during summer, thus the seasonal temperature effects to TTHM formation were not assessed. Hence, there were no observations indicating changes in water temperature to TTHM formation because the temperatures of the samples were very similar. Similarly, Ye *et al.* (2009) also observed no correlation between TTHM formation and water temperature. In addition, Loyola-Sepulveda *et al.* (2013) performed a study on water samples in Central Chile during summer of 2007 and autumn-winter of 2008. From the results obtained, temperature was not a major factor in the THM concentrations at the point of use although lower overall concentrations were measured in summer. This might also have indicated that THMs as VOCs might have escaped during sampling, particularly for summer months, which are generally warmer, when compared to winter months. In conclusion, in the current study the correlation between TTHM formation and water temperature was not assessed for the samples collected from the various treatment plants as only one season was studied and the variation among the plants was minimal.

Summary

The average TTHM concentrations detected in the treated drinking water from seven of the drinking water treatment plants (DWTP) and one drinking water distribution station (DWDS) of the Western Cape, were in the low ranges and were comparable for seven of the water treatments plants, for both the concentration of the TTHM and the individual THM species, namely chloroform, bromoform, dibromochloromethane and bromodichloromethane. Chloroform was detected in all the various water treatment plants. The only notable concern was for the TTHM results obtained for the Atlantis DWTP, for which high concentration of TTHMs were above 100 µg/L in two of the three water samples, resulting in an average TTHM concentration of 83.48 µg/L. The individual concentrations of the THM species were also very high for Atlantis compared to the other water treatment plants. However, the average TTHM concentrations and the concentrations of the individual THM species for all the DWTP and the DWDS were below the SANS and WHO drinking water guideline limits. Therefore, monitoring arrangements need to be in place for the Atlantis water treatment plant.

Furthermore, the average residual free chlorine concentration for Atlantis was very low (0.06 mg/L), which is even below the WHO minimum residual free chlorine concentration guideline value of 0.2 mg/L for the distribution network.

pH was shown to have no effect on TTHM formation and these findings were consistent with observations from several research studies. Similarly, there was no correlation between TOC and TTHM formation. This was due to the fact that the TOC concentrations for the various treatment plants were quite low and very similar, hence there was a limited distinct trend. The conclusion deduced from this study was that the effect of TOC on THM formation is insignificant at low TOC concentrations. This was also observed for temperature as there were no seasonal changes, i.e. all the samples were collected during summer, and also the temperatures of the water samples from the various drinking water treatment plant were similar. Therefore, the effects of temperature on THM formation were not assessed.

A trend was observed indicating that for most of the water treatment plants, a higher chlorine dose resulted in a higher chloroform formation. Furthermore, residual free chlorine decreased through the distribution network. The average residual free chlorine concentrations in seven of the water treatment plants were in the range 0.06 to 1.06 mg/L. The residual free chlorine concentrations from the tap water outlets was also determined to be very low, ranging from 0.02 to 0.06 mg/L, with low THM concentrations (specifically chloroform) observed compared to the levels obtained in water from the water treatment

plants. This concentration was below the WHO guideline value of 0.2 mg/L at the point of delivery. Drinking water treatment utilities in the region might need to develop a strategic plan to introduce post-chlorination stations along the distribution network. This is to ensure that a chlorine residual of 0.2 to 0.3 mg/L is maintained through the distribution network and a concentration of 0.2 mg/L is detected at the consumer's tap.

5.2 Perfluorinated compounds (PFCs) in raw and treated drinking water sources of the Western Cape, South Africa

The guidelines values issued by USEPA for PFOA and PFOS were 400 and 200 ng/L, respectively. Thus, the primary objective of this study was to focus on the detection of PFCs in drinking water sources of the Western Cape, other than PFOA and PFOS. The aim was to determine whether these PFCs would be detected in concentrations above the USEPA guideline values. PFC analysis was only performed in raw and treated water from seven DWTPs and one DWDS, and tap water was not analysed. Furthermore, the study of health effects of these PFCs is beyond the scope of this study.

The average PFC concentrations detected in this study are presented in Table 5-7. For the purpose of this study, the limit of quantification (LOQ) was set at 0.2 ppm for PFOA and PFOS and at 0.1 ppm (100 µg/L) for other PFCs, with the reasoning that any PFCs detected above these limits would indicate a widespread public health concern. The foundation for this is based on the literature reviewed. From the studies performed on PFCs and as seen in more than 70% of the literature reviewed during this study, most researchers focused on PFOA and PFOS, their presence in water sources and their detrimental health effects to humans and living organisms with substantially less attention given to the other PFCs.

Table 5-7: Concentrations of perfluorinated compounds detected above the LOQ (100 µg/L) in drinking water sources of the Western Cape

Sample	FINAL CONCENTRATION (ng/L)						
	PFHpA	PFDoA	PFNA	PFUA	PFOA	PFDeA	PFOS
Faure raw	24.19	4.415	1.880	2.161	0.230	2.744	<LOD
Faure final	27.720	1.963±1.55	2.086	0.698	<LOD	1.020±0.62	<LOD
Brooklands raw	<LOD	1.897	0.757	0.475	<LOD	0.781	1.082±0.68
Brooklands final	0.271	10.410	1.506	7.965	<LOD	1.531	1.118±0.65
Voelvlei raw	<LOD	1.754	<LOD	<LOD	<LOD	<LOD	<LOD
Voelvlei final	<LOD	1.825	<LOD	0.799	<LOD	<LOD	<LOD
Steenbras raw	27.130	1.947±0.96	0.061	<LOD	<LOD	0.480	<LOD
Steenbras final	39.518	3.202±0.36	1.973	1.277	<LOD	0.935	<LOD
Wemmershoek raw	22.671	0.943	1.507	4.488	<LOD	2.617	<LOD
Wemmershoek final	38.825	3.337±0.97	2.862	2.271	<LOD	1.337	<LOD
Atlantis raw	<LOD	2.562±2.09	<LOD	<LOD	<LOD	<LOD	<LOD
Atlantis final	<LOD	0.579	<LOD	<LOD	<LOD	<LOD	<LOD
Blackheath raw	<LOD	0.384	<LOD	<LOD	<LOD	<LOD	<LOD
Blackheath final	<LOD	4.032	1.140	1.798	<LOD	1.525	<LOD
Plattekloof inlet	37.478	1.818	2.639	0.532	<LOD	1.812	<LOD
Plattekloof outlet	43.804	1.328	2.922	1.906	<LOD	1.465	<LOD

Perfluorooctanoic acid (PFOA); Perfluorooctane sulfonate (PFOS); Perfluoroheptanoic acid (PFHpA); Perfluorododecanoic acid (PFDoA); Perfluorononanoic acid (PFNA); Perfluoroundecanoic acid (PFUA); Perfluorodecanoic acid (PFDeA).

LOD – Limit of detection

From the literature reviewed, a precautionary value for PFOA and PFOS of 5000 ng/L was set by the German Drinking Water Commission and this amount was tolerable for 1 year of water consumption, whereas in the United Kingdom, the Drinking Water Inspectorate of England and Wales issued guideline values for PFOS and PFOA ranging from 300 to 9×10^3 ng/L for PFOS and 300 to 9×10^4 ng/L for PFOA. Furthermore, New Jersey had a guideline limit value of 40 ng/L for PFOA (Rumsby *et al.*, 2009). It is clear that these values ranged from more conservative to less conservative from country to country, ranging from 40 ng/L for PFOA to a maximum of 9×10^3 ng/L (for PFOA), and 9×10^4 ng/L (for PFOS). Evidently, from the studies performed thus far on PFCs, there is no concrete limit value and no conclusive evidence existing to prove that PFCs cause toxic effects at certain concentrations. Most countries chose these values to suit their drinking water regulations.

To substantiate this statement, in a study by Huang *et al.* (2010) tests were performed in living organisms such as zebrafish embryos. These embryos were exposed to PFOS concentrations as high as 8 mg/L (8×10^6 ng/L) to observe abnormality defects in development due to PFOS. Results showed that PFOS was developmentally toxic in all windows of development and it accumulated in the zebrafish embryos with minimal elimination (Huang *et al.*, 2010). Furthermore, a study by Stahl *et al.* (2009) involved tests that were performed in plant organisms and results showed that various crop plants indicated visible abnormalities at soils with PFOS and PFOA concentrations of 0.25 to 50 mg/kg, respectively (Stahl *et al.*, 2009). In addition, toxic effects of PFOS were only visible at PFOS concentrations greater than 10 mg/L (Qu *et al.*, 2010). What can be deduced from these findings is that from the majority of tests performed, toxic effects of PFCs were mostly evident at high concentrations (i.e. in the ppm range).

For the purpose of this study, the limit of quantification was 0.2 mg/L (200 µg/L) for PFOA and PFOS, and 0.1 mg/L (100 µg/L) for other PFCs. From the results obtained in this study (Table 5-7), five different PFCs (i.e. PFHpA, PFDoA, PFNA, PFUA and PFDeA) were detected in raw and treated water above the limit of quantification of 0.1 mg/L (100 µg/L). Most of these PFCs were detected in both raw and treated water, with perfluoroheptanoic acid (PFHpA) being the most prevalent PFC detected in treated water, with a maximum average concentration of 43.80 ng/L (Plattekloof) above the LOQ. The highly researched and reported Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS) were not detected above the LOQ of 0.2 mg/L in numerous samples and overall, they were the least detected PFCs; both detected in only one treatment plant. The average concentrations were 0.230 ng/L for PFOA (for Faure raw water), and 1.082 ng/L and 1.118 ng/L for PFOS (for Brooklands raw and treated water, respectively). Another observation from the results was that the majority of PFC concentrations detected in treated water were higher than those

observed in raw water. Similar results were observed by Oilaei *et al.* (2006) where PFCs were removed by granular activated carbon treatment. PFOS and PFOA were removed in high rates whereas some PFCs increased after the treatment. However, in this study, the treatment methods for the various DWTPs were not studied; hence, the increase in these PFCs cannot be justifiably explained due to insufficient information.

In conclusion – the results obtained in this study indicate that PFCs, including PFOA and PFOS, are present in drinking water sources of the Western Cape, and that these PFCs occur in concentrations higher than the guideline limit values set for PFOS and PFOA. That is, they occur in concentrations above the high LOQ of 0.1 mg/L, higher than the guidelines values of 200 ng/L (PFOS) and 400 ng/L (PFOA). This means that future regional and national studies should give attention to PFCs identified in this study because these PFCs are present in high concentrations in drinking water of the Western Cape. This suggested that the use of materials in the DWTP might have contributed to the possible contamination of the drinking water.

Summary

The primary objective of this section of the study was to analyse and quantify PFCs in drinking water sources of the Western Cape, other than PFOA and PFOS. The aim was to determine whether PFCs would be detected in concentrations above the USEPA guideline values. From the results obtained, seven PFCs, including PFOA and PFOS, were detected in raw and treated water sources in seven DWTPs and one DWDS of the Western Cape, South Africa. These PFCs were detected in concentrations above the limit of quantification of 0.1 mg/L and 0.2 mg/L for PFOA and PFOS. Furthermore, it was observed from the majority of the results that treated water had higher PFC concentrations as compared to raw water, which might be due to possible contamination. Lastly, these results highlighted the predominance of all PFCs in drinking water sources such that future studies should not only focus on PFOA and PFOS, particularly in South Africa. Once more, the WHO and the SABS must consider establishing guideline values for these PFCs for continuous monitoring.

CHAPTER 6

OVERALL DISCUSSION AND CONCLUSION

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6.1 Overall Discussion

6.1.1 Trihalomethanes

Trihalomethanes are disinfection by-products, which are formed when chlorine reacts with natural organic matter in water. Although chlorination of drinking water has been and is still presently the most common, cost effective, reliable and convenient procedure used for water treatment worldwide, its disadvantage is that it produces trihalomethanes which are linked with possible adverse health effects associated with chronic exposure to chlorination disinfection by-products (DBPs). All the chlorinated DBPs are equally important, but the focus for the current study will be on THMs due to the fact that they have raised significant concern as a result of the evidence of their association with potential adverse human health effects, including pancreatic and bladder cancer (Do *et al.*, 2005) and reproductive and developmental effects (Reif *et al.*, 1996). Furthermore, THMs occur at higher levels than any other known DBPs and their presence in treated water is representative of the occurrence of many other chlorination DBPs (USEPA, 2005). Since water plays a vitally important role in our lives and water scarcity is presenting a significant challenge in South Africa, it is imperative that the quality of our water resources is regulated and monitored closely. The primary objective of this study was thus to analyse and quantify trihalomethanes in chlorinated drinking water, from seven drinking water treatment plants (DWTPs): Atlantis, Blackheath, Faure, Brooklands, Steenbras, Voelvlei and Wemmershoek, and one drinking water distribution station (DWDS) at Plattekloof, of the Western Cape and from tap water collected from several of the Western Cape suburbs including townships to assist local authorities in contributing to the development and improvement of water quality standards in the country. The effects of various parameters on TTHM formation were also assessed.

From the results obtained, the average TTHM concentrations were in the low ranges and quite comparable for seven of the water treatment plants, ranging from lowest 26.52 ug/L (for Plattekloof) to 32.82 ug/L (for Brooklands). The only outlier was the Atlantis water treatment plant, having the highest concentration of 83.48 ug/L. In comparing the individual THM concentrations, chloroform was dominant of the four THM species assessed in all the water treatment plants, with average concentrations ranging from 11.74 ug/L for Plattekloof to 46.06 ug/L for Atlantis. Dibromochloromethane (DBCM) was the least detected of the species, with average concentrations ranging from 1.00 µg/L (for Voelvlei) to a highest average concentration of 4.94 µg/L (for Atlantis). From these results, it was evident that THMs are present in drinking

water sources of the Western Cape. Furthermore, compared to other studies in other countries, these concentrations were well within the guideline limits governing our water quality (i.e. SANS and WHO). The only concern was the water quality of the Atlantis treatment plant, as it had the highest concentrations for each of the four THM species compared to the other seven water treatment plants. More tests are therefore required and the source of the THMs needs to be investigated and identified.

From previous studies on THMs, it was discovered that several parameters affect the formation of THMs in drinking water sources, such parameters as water pH, water temperature, natural organic matter, and chlorine dose. pH levels in the water samples have shown to have no effect on TTHM formation (i.e. there was no correlation between the two), findings which were consistent with observations from some of the researchers. The pH was not adjusted to different levels as this study was only focusing on the characteristics of the water as they are from the treatment plants; therefore, not much effect on THM formation was observed from water pH due to the fact that all the samples had similar pH values.

Another parameter that was assessed was NOM, considered the most important precursor of THMs formation but having no direct measurement. It was therefore quantified as TOC in water. The results obtained in this study revealed, TOC was present in low concentrations in the water samples - thus there was a correlation between TOC and TTHM formation but it was less significant. This was because the TOC concentrations for the various treatment plants were quite low and very similar. Consequently, there was no distinct trend. This might also be attributed to the different organic matter in water, their different chemical properties, and the fractions in which they are present in water. Some organic substances have high DBP formation potential compared to others, and some occur in larger fractions than others. However, this study did not investigate the types and characteristics of the different organic substances that were present in the water samples. These findings were however comparable with the findings of Ye *et al.* (2009), whereas other researchers found a distinct correlation between the two factors.

From chlorine tests, a trend was observed indicating that for most of the water treatment plants, a higher chlorine dose resulted in a higher chloroform formation. Furthermore, residual free chlorine decreased through the distribution network. The average residual free chlorine concentrations in all seven of the water treatment plants were in the range of 0.06 to 1.06 mg/L.

The residual free chlorine concentrations from the tap water outlets were very low, ranging from 0.02 to 0.06 mg/L, resulting in low THM concentrations (specifically chloroform) compared to the levels obtained in the water treatment plants. This might be because chlorine decreases with time in a water-based medium, as it is volatile and can react with other constituents in the water to form other by-products. This residual free chlorine can react with water constituents such as corrosion by-products, microorganisms, organic impurities, ammonia-based compounds, etc., leading to its consumption thus minimal detection in chlorinated water. Additionally, it was determined that free chlorine is largely used up by reactions with biofilms formed on the distribution pipe walls (Karim *et al.*, 2011). This concentration was below the WHO guideline value of 0.2 mg/L at the point of delivery. Drinking water treatment utilities thus need to ensure that after chlorination, the residual free chlorine concentration is ≥ 5 mg/L after a contact time of at least 30 minutes at pH < 8. This is to ensure that a chlorine residual of 0.2 to 0.3 mg/L is maintained through the distribution network and a concentration of 0.2 mg/L is detected at the consumer's tap.

The last parameter which has an effect on THM formation is water temperature. From the results obtained in the current study, the water samples were only collected during summer, thus the seasonal temperature effects to TTHM formation were not assessed. Hence, there were no observations indicating changes in water temperature to TTHM formation because the temperatures of the water samples from the various drinking water treatment plants were very similar.

6.1.2 Perfluorocarbons

Perfluorinated compounds (PFCs) are drinking water contaminants which are equally detrimental to human health as THMs. Perfluorinated compounds (PFCs) are persistent, bio-accumulative and toxic fluorine-based chemicals (Skutlarek *et al.*, 2006), which do not occur naturally as they are degradation products of many man-made perfluorinated compounds used in consumer and industrial applications. This means that PFCs are abundant in the environment and can affect the quality of our water resources. The primary concern that led to the implementation of this study was the fact that the majority of studies focused only on two PFC contaminants in drinking water, namely PFOS and PFOA, neglecting other PFCs. Another reason was that while PFCs have been detected in drinking water sources worldwide, they have not previously been detected in South African drinking water. This study focused on the detection of PFCs in drinking water sources of the Western Cape, other than PFOS and PFOA.

From the results obtained, it is clear that PFCs are present in our drinking water sources in higher concentrations and that they are not being monitored. The national drinking water standard (SANS 241) and international drinking water guidelines (WHO) governing the quality of drinking water do not mention any PFCs. Furthermore, despite the vast number of studies that have been performed around the world and with so much knowledge on the detrimental effects of these PFCs to human health, there is still no mention of these in the drinking water standards. The greatest concern is that individuals may be exposed to high levels of PFCs via drinking water as these compounds are water soluble, and so conventional water treatment systems and processes may not eliminate these compounds completely (Takagi *et al.*, 2008). Due to minimal monitoring and the dearth of legislated regulations regarding PFCs in the water sector of South Africa, the prevalence and presence of these fluorochemicals is largely unreported. In addition, in a study performed by Hanssen *et al.* (2010), perfluorinated compounds were detected for the first time in maternal serum and cord blood of pregnant women at 1.6 ng/mL for PFOS and 1.3 ng/mL for PFOA, with the PFOS being the most abundant compound (Hanssen *et al.*, 2010). Surely, that should raise concerns for the water regulations to have a closer look at these PFCs but thus far, nothing has happened. The latest issue of SANS 241 was released in 2011 but still without mentioning of any of the PFCs. The results obtained from this study will help provide guidance in terms of regulating water quality in the Western Cape and emphasis that future studies must give more attention to all PFCs, as they are largely water-soluble.

6.2 Overall Conclusion

Water plays a major role in our lives and our water resources need to be managed in a manner that ensures their sustainability. In South Africa, rivers and dams are the main sources of water but the quality of this water remains threatened by the increasing amount of contaminants to which our environment is exposed. According to the literature reviewed, there is inadequate monitoring of contaminants in drinking water sources in South Africa compared to other countries. Yes, there are guideline limits for THMs in the SANS but these are not continuously monitored and their levels in water are not known. The results obtained in this study show that THMs occur in low concentrations in drinking water but at such levels which necessitate that these concentrations should be checked continuously and with precision. The residual free chlorine results from the tap water were within the specification limits stipulated in SANS 241:2011 but were below the WHO limit of 0.2 mg/L, showing the SANS to be less stringent when it comes to water quality and its potential effects to human health. This also highlights the fact that drinking water treatment utilities need to ensure that after chlorination, the residual free chlorine concentration is ≥ 5 mg/L after a contact time of at least 30 minutes at

pH < 8. This is to ensure that a chlorine residual of 0.2 to 0.3 mg/L is maintained through the distribution network. If the residual free chlorine is below this concentration, this might lead to very low or no chlorine in the farthest part of the distribution system as well as the consumer's taps, which may result in high risk of bacterial contamination of drinking water.

Finally, PFCs results showed the presence of PFCs in the drinking water sources of the Western Cape. Seven PFCs were detected in raw and treated water sources in seven DWTPs and one DWDS of the Western Cape South Africa. These PFCs were detected in concentrations above the limit of quantification of 0.1 mg/L and 0.2 mg/L for PFOA and PFOS, respectively. The emphasis is thus on future studies to not focus only on PFOA and PFOS, but also for the WHO and the SABS to consider having guideline values for all PFCs in drinking water sources.

6.3 Recommendations for future studies

This study reported on the primary objectives, which were the detection and quantification of trihalomethanes (THMs) and perfluorinated compounds (PFCs) in drinking water sources. In order to improve monitoring of the contaminants in water resources, the following need to be investigated further:

- Effective methods for the reduction of THM precursors.
- Effective methods for the reduction of THMs in chlorinated water.
- Detection of other DBPs in drinking water sources of the Western Cape.
- Other effective disinfection methods that will result in small amount of or less harmful DBPs.
- Sources of PFCs.
- Effects of the different water pre-treatment methods on PFC concentrations.
- Effective treatment methods for PFCs in drinking water sources; and
- Potential human health effects (e.g. testing of blood samples) resulting from THMs and perfluorinated compounds contamination exposures in the Western Cape.

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