NATURAL ORGANIC MATTER (NOM) QUANTITY AND QUALITY; INNOVATION IN CHARACTERIZATION, MEASUREMENT AND MONITORING OF NOM IN SOUTH AFRICAN WATER SYSTEMS

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by

SAVIA SUSANNA MARAIS

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Supervisor	**:**	**Prof Bhekie B Mamba**
Co-supervisors	**:**	**Dr Esper J Ncube**
		Prof Titus AM Msagati
		Dr Thabo TI Nkambule

November 2018

DECLARATION

Name: Savia Susanna Marais

Student number: 45089841

Degree: PhD

I declare that this thesis is my own work and all sources quoted or used were indicated and acknowledged by complete references.

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SIGNATURE DATE

DEDICATION

I dedicate this study to each and every person in South Africa who did not get the opportunity of experiencing the effort, enrichment and gratitude of being involved in a post graduate study.

"I never lose. I either win or learn" – Nelson Mandela

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Peer-reviewed Publications

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- S. S. Marais, E. J. Ncube, T. A. M. Msagati, B. B. Mamba and T. I. Nkambule. (2018) Comparison of Natural Organic Matter Removal by Ultrafiltration, Granular Activated Carbon Filtration and Full Scale Conventional Water Treatment. *Journal of Environmental Chemical Engineering*. 6 (5), 6282-6289.

- S. S. Marais, E. J. Ncube, T. A. M. Msagati, B. B. Mamba and T. I. Nkambule. (2018) Assessment of trihalomethane (THM) precursors using specific ultraviolet absorbance (SUVA) and molecular size distribution (MSD). *Journal of Water Process Engineering.* Under review. JWPE_2018_402.

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- S. S. Marais, E. J. Ncube, T. A. M. Msagati, B. B. Mamba and T. I. Nkambule. *Seasonal NOM quantity and quality: The influence of NOM character on THM formation.* Oral presentation. Water Research Commission (WRC) Workshop on natural organic matter (NOM) in South African waters, University of Kwa-Zulu Natal (KZN), Durban, South Africa, 9 June 2017.

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- S. S. Marais, E. J. Ncube, T. A. M. Msagati, J. Haarhoff, T. I. Nkambule and B. B. Mamba. *Characterisation and removal of natural organic matter by a conventional water treatment plant in South Africa.* Poster presentation. Poster presentation. 4th Young Water Professionals (YWP) South African (ZA) Biennial and 1st African YWP Conference, 16 - 18 November 2016, Pretoria, South Africa.

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- S. S. Marais, E. J. Ncube, T. A. M. Msagati, T. I. Nkambule and B. B. Mamba. *Characterization and removal of natural organic matter by a water treatment plant in South Africa*. Oral presentation. International Water Association (IWA) Specialist Conference on Natural Organic Matter in Drinking Water, Malmö, Sweden, 7 - 10 September 2015.

Technical Reports

- S. S. Marais, N. G. Ndlangamandla, D. A. Bopape, W. F. Strydom, W Moyo, N. Chaukura, A. T. Kuvarega, L. de Kock, B. B. Mamba, T. A. M. Msagati and T. I. Nkambule. (2018) Natural organic matter (NOM) in South African waters.
  Volume I: NOM fractionation, characterization and formation of disinfection by-products. Report No. K5/2468/3, Water Research Commission, South Africa, 2018.
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ABSTRACT

During potable water treatment ineffectively removed natural organic matter (NOM) intensifies the challenge to prevent trihalomethane (THM) formation when NOM reacts with the disinfectant to form disinfection by-products (DBPs). Owing to the limited information on NOM quantity and quality within South African surface waters, NOM is identified as a significant concern during drinking water treatment. Although it has been established that NOM is the main precursor responsible for the formation of THMs during chlorination, the individual NOM fraction responsible for THM formation at Rand Water (the largest bulk water utility in South Africa) has to date not been identified. The aim of this study was therefore to characterize NOM using advanced NOM characterization techniques using an improved biodegradable dissolved organic carbon (BDOC) technique, while incorporating these techniques in a NOM characterization and monitoring protocol. It was envisaged that such an investigation would enable the treatability of the individual NOM fractions to be determined and thus establish their influence on the THMs formed in the water systems of Rand Water.

Following fractionation using the modified polarity rapid assessment method (m-PRAM), characterization of the hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) fractions using molecular size distribution (MSD), BDOC, dissolved organic carbon (DOC), UV_{254} and specific ultraviolet absorbance (SUVA) measurements were undertaken. In order to assess any changes in the fluorescence intensity (FI) of each NOM fraction during the chlorination process and thus identify the components contributing to THM formation, additional fluorescence excitation emission matrix (FEEM) analyses were included in the trihalomethane formation potential (THMFP) investigation.

Variability in the quantities of HPO, HPI and TPI during the various seasons investigated over a period of four years suggests that NOM characterization and monitoring should occur on an on-going basis. Seasonal NOM characterization has revealed that as the DOC of the source water increases during high flow seasons (on average from 5.1 mg/L to 5.6 mg/L during years 1 to 4) and aromaticity (SUVA) decreases, TTHM formation in the final treated water increases (from 46.1 µg/L to 64.6 µg/L). When the source water UV_{254} ranged between 25 m^{-1} and 45 m^{-1} and the corresponding SUVA were above 4 L/mg.m, subsequent UV_{254} removal by the full scale plant ranged between 60% and 80%.

This reveals that removal of NOM is not completely affected by seasonal rainfall and temperature changes but to a greater extent by the bulk organic loading.

An evaluation of the MSD of NOM using high performance size exclusion chromatography (HPSEC) revealed that THM formation is largely influenced by the presence of high molecular weight (HMW) NOM in Vaal Dam source water. This was illustrated by a correlation coefficient value of 0.9633 ($p < 0.05$) between chloroform and HMW NOM (Peak I), showing that chloroform-based THM formation occurring in the summer months was primarily of HMW (aromatic) NOM origin. A THMFP of 39.1% of the HPO NOM (35%) fractionated in the source water using m-PRAM, shows that the HPO fraction within this oligotrophic source water has the highest propensity to form THMs. FEEM results seem to suggest that chlorine is most likely to react with humic and proteinaceous substances within the HPO NOM fraction since the humic acid-like (Region V) and protein-like (Region II) materials were reduced during chlorination by area volumes of 31.2% and 57.5%, respectively.

An innovative aspect of this research involves the development of an enhanced BDOC technique whereby the period of the experimental method was shortened from an original 6 day period to 4 days. As evidenced by BDOC levels of 41.9%, which were achieved for HPO NOM (in comparison to 35.3% and 34.5% levels achieved for the respective fractions of TPI and HPI), the enhanced-BDOC technique was utilised to demonstrate the amenability of the HPO fraction towards heterotrophic bacterial degradation.
Most importantly, the characterization protocol developed in this work (i.e. m-PRAM, e-BDOC, THMFP and FEEM) enabled the identification of the HPO NOM fraction as the problematic fraction. Noteworthy, the problematic fraction refers to the fraction with the highest THMFP that is not effectively removed by the water treatment plant (WTP), more degradable by bacteria thus subsequently being responsible for the formation of biofilms in the distribution system.

In conclusion, it is envisaged that this NOM characterization protocol will benefit the water industry immensely by proposing a series of existing advanced NOM characterization tools and the improved 4 day biodegradability technique that will confidently identify the problematic NOM fraction, within a shorter turnaround time. In addition, the application of the proposed protocol will inaugurate a sound perception of the role that the individual NOM fractions play during disinfection at potable water treatment plants.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

BAC	Biological Activated Sand
BDCM	Bromodichloromethane
BDOC	Biodegradable Dissolved Organic Carbon
C18	Octadecylsilane
CN	Cyanopropyl
DBCM	Dibromochloromethane
DBP(s)	Disinfection by-product(s)
DOC	Dissolved Organic Carbon
EEM	Excitation Emission Matrix
FEEM	Fluorescence Excitation Emission Matrix
FI	Fluorescence Intensity
FRI	Fluorescence Regional Integration
GC	Gas Chromatography
GC-ECD	Gas Chromatography-Electron Capture Detector
HANs	Haloacetonitriles
HMW	High Molecular Weight
HAA(s)	Haloacetic acid(s)
HAAFP	Haloacetic Acid Formation Potential
HNMs	Halonitromethanes
HPI	Hydrophilic
HPIA	Hydrophilic acids
HPIB	Hydrophilic bases
HPIN	Hydrophilic neutrals
HPLC	High Performance Liquid Chromatography
HPO	Hydrophobic
HPOA	Hydrophobic acids
HPOB	Hydrophobic bases
HPSEC	High Performance Size Exclusion Chromatography
IMW	Intermediate Molecular Weight
LMW	Low Molecular Weight
mAU	Milli-Absorption Units
m-PRAM	Modified Polarity Rapid Assessment Method
MSD	Molecular Size Distribution

M_w	Molecular weight
MQW	Milli-Q Water
NDMA	N-nitrosodimethylamine
NH_2	Aminopropyl
NOM	Natural Organic Matter
ParaFac	Parallel Factor
PACl	Poly Aluminium Chloride
PRAM	Polarity Rapid Assessment Method
RW	Rand Water
SEC	Size Exclusion Chromatography
SPE	Solid Phase Extraction
SANS	South African National Standards
SUVA	Specific Ultraviolet Absorbance
THM(s)	Trihalomethane(s)
THMFP	Trihalomethane Formation Potential
TOC	Total Organic Carbon
TPI	Transphilic
TTHM	Total Trihalomethane
UV_{254}	Ultra Violet absorbance at wavelength of 254 nm
WHO	World Health Organization
WRC	Water Research Commission
WTP	Water Treatment Plant

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Natural organic matter (NOM) in water emanates primarily from the decay and resultant leaching of organic materials of plant, animal and microbial origin (Page *et al*., 2002a). In its natural environment, NOM is not a concern. However, during drinking water treatment, NOM gives rise to potable water of reduced quality caused by the formation of disinfection by-products (DBPs) during the disinfection step (Özdemır, 2014). Other impacts associated with insufficient removal of NOM during potable water treatment include microbial regrowth in the distribution pipelines as well as objectionable taste- and unpleasant odour-causing agents, which are also responsible for the coloration (usually yellowish) of the final water (LeChavelier *et al*., 1991).

NOM can be defined as an intricate blend of organic components and, although their composition differs within water bodies, they are present in all natural water systems. NOM can mainly be divided into humic (hydrophobic) and non-humic (hydrophilic) material with the major component of NOM being humic substances. Humic substances are derived from soil or produced by chemical and biological processes (Page *et al*., 2002a). Humic substances are of low to moderate molecular weight and have both aliphatic and aromatic components (Letterman *et al*., 1999). NOM can be further divided into hydrophilic (HPI), transphilic (TPI) and hydrophobic (HPO) NOM fractions with hydrophobic referring to humic substances having a higher aromaticity (Edzwald & Van Benschoten, 2010).

Due to NOM being a composite mixture having a polydisperse and irregular structure (Hertkorn, 2006), separation of NOM based on hydrophobicity has been the focus of several studies (Leenheer, 1981, Rosario-Ortiz *et al*., 2007; Piper *et al*., 2010). NOM characterization is also made difficult by the fact that organic matter does not have a homogenous organic matrix, but is a mixture of divergent size, structure and functionality. To overcome this limitation the use of various measurement and characterization techniques are required to allow for reliable identification of NOM. Another limitation, which relates to the treatability of NOM by conventional water treatment (i.e. coagulation, filtration,

sedimentation, and chlorination) not being well understood, serves as further motivation for undertaking this study.

1.2 PROBLEM STATEMENT

Within the potable water industry the following key problems associated with the incomplete NOM removal during the conventional water treatment processes are well known:

i. biofilm formation within the distribution pipelines (due to bacterial regrowth); and
ii. formation of unwanted DBPs in the final drinking water due to the reaction of insufficiently removed NOM with disinfectants during the disinfection stage of water treatment.

Therefore, it suffices to say that there is a general recognition within the water industry of the importance of NOM monitoring, characterization and removal during potable water treatment. However, the assessment of NOM character conducted in South African water supply systems is limited (Nkambule, 2012). In addition, currently available NOM characterization methods have various limitations emanating from the NOM structure that changes seasonally (Sharp *et al*., 2006) as well as the NOM composition that varies throughout different geographical areas (Nkambule *et al*., 2011).

The intrinsic heterogeneous mixture of NOM poses a serious challenge, and various methods of characterization are needed to ensure all of its structural and functional properties are quantified. Although various organic matter measurement techniques are available, a single technique only provides partial information on the overall NOM quantification and a combination of these techniques is therefore usually required.

In potable water treatment it is also imperative to monitor and characterize NOM since:

a) the amount and composition of organic matter in source water affects the efficiency of the water treatment process (Sharp *et al*., 2006; Kristiana *et al*., 2011);
b) different chemical properties of NOM are removed by different treatment processes (Parsons *et al*., 2004);
c) certain NOM fractions (based on their polarity and molecular weight distribution) are more amenable to removal during water treatment than other fractions (Chang *et al*. 2004, Van Leeuwen *et al*., 2005);
d) incomplete NOM removal adversely affects the final water quality; and

e) a more in depth understanding is necessary regarding NOM properties and bacterial degradation of NOM (Young, 2005).

In order to address current full scale NOM characterization needs in South African potable water treatment plants, the outcome of this study will provide a fail-safe NOM characterization technique that can be utilised on source waters containing different NOM quantity and quality. Not only will this method identify the problematic NOM fraction, it will also provide some insight into the relationship between the bacteria existing within the treatment process and the NOM character of the source water.

Characterization of NOM in the surface water from the Vaal Dam within Rand Water's catchment area will provide some insight into the monitoring of NOM and the efficiency of the full scale conventional water treatment plant in terms of NOM removal. Attempts will also be made to provide information on the relationship between the various chlorinated DBPs formed within the final drinking water and the individual HPO, HPI and TPI NOM fractions within the Vaal Dam source water.

A NOM removal strategy is expected to be developed by incorporating NOM characterization and treatability as well as DBP formation. This strategy is specifically aimed at optimisation of the treatment process, which will lead to the enhancement of NOM removal as well as the reduction of DBPs formed in the final drinking water.

1.3 JUSTIFICATION

1.3.1 Fate and occurrence of NOM during potable water treatment

NOM is present in all natural water systems and it adversely affects the final water quality if it is not inadequately removed during potable water treatment. Due to surface water generally containing a higher concentration of NOM with different composition than groundwater, a more effective treatment regime is required to remove NOM prior to disinfection when using surface water for potable water treatment (Gallard & Von Gunten, 2002, Howe *et al*., 2012). Impaired water quality due to insufficient removal of NOM includes odour, taste and colour problems and also producing chlorinated DBPs in the final treated water when residual NOM reacts with the disinfectant (i.e. chlorine) (Frimmel & Jahnel, 2003). The easily biodegradable NOM fractions promote bacterial growth in the distribution system; these bacteria utilise NOM as a food substrate (Page *et al*., 2002b; Baghoth *et al*.,

2009). Therefore, not only will bacterial growth lead to increased biofilm formation and growth within the water distribution network, the quality of the water supplied to the consumer is severely compromised (Van der Kooij, 1992).

1.3.2 Characterization of NOM

Water from one of the biggest dams in South Africa, the Vaal Dam, is abstracted by a bulk potable water utility (Rand Water), which provides on average 3 653 million litres of water per day to more than 12 million consumers (Ncube *et al*., 2012). Other than the problem of inconsistent NOM composition in South African water treatment plants, little is known regarding the occurrence, concentration and nature of NOM in the Vaal Dam surface water system (Nkambule *et al*., 2011). Since different NOM fractions are responsible for the formation DBPs (Hassouna *et al*., 2014, Özdemır, 2014), the amount and composition of source water NOM affects the efficiency of water treatment plants (Sharp *et al.,* 2006) and different NOM fractions are reduced by different treatment processes (Parsons *et al*., 2004), it is important that the NOM in the Rand Water source water is characterized first. The characterization will allow for optimal removal of the problematic NOM fractions and enable the DBP precursor removal process to be optimised.

Characterization of NOM entails the isolation and fractionating of NOM into minor fractions using various characterization techniques. Advanced characterization methods available for the fractionation of organic matter include the polarity rapid assessment method (PRAM), a modified PRAM (m-PRAM) (Nkambule, 2012), high performance size exclusion chromatography (HPSEC), fluorescence excitation-emission matrices (FEEM) and biodegradable dissolved organic carbon (BDOC) measurement. Parameters used to characterize NOM include ultraviolet (UV) absorbance analysis at a 254 nm wavelength, specific ultraviolet absorbance (SUVA) analysis as well as dissolved organic carbon (DOC) measurements, which provide information on the aromaticity and amount of humic substances within the organic matter.

The PRAM fractionation procedure is used to determine the polarity of NOM by evaluating the quantity of material adsorbed onto various solid-phase extraction (SPE) sorbents (Rosario-Ortiz *et al*., 2007). The PRAM method is used to predict any change in the polarity of NOM during water treatment and is also a very valuable technique to assess and thus optimise process efficiency and removal of NOM.

The HPSEC is a reproducible, relatively fast technique that divides NOM graphically into six peaks representing the humic fractions ranging from high to low molecular weight and the percentage of each NOM fraction (Pelekani *et al*., 1999; Nissinen *et al*., 2001). It is well recognised that the high molecular weight (HMW) component represents the humic and fulvic acid compounds and the low molecular weight (LMW) fraction represents the non-humic fractions (Szabó & Tuhkanen, 2007). The change in the molecular weight distribution throughout the water treatment process can also be used to indicate NOM removal after each treatment step (Vuorio *et al*., 1998; Matilainen *et al*., 2002).

Another advanced NOM characterization tool, the FEEM, can be used to predict the type and quantity of organic matter in a sample (Roe, 2011; Baghoth, 2012), as the composition and concentration of organic matter influences the intensity and shape of the fluorescence spectra (Coble, 1996). The locations of fluorescence intensity peaks and FEEM contour plots can thus be used to predict the type of organic matter, being humic-, fulvic- or protein-like material (Coble, 1996). ParaFac analysis can be used for the prediction of DBP formation by using fluorophore component scores in the evaluation of DBPs (Johnstone, 2009).

The UV absorbance measured at a wavelength of 254 nm (UV_{254}) is a rapid measurement tool that is accessible to water treatment plant personnel (Lobanga *et al*., 2014) and it provides information on the aromatic organics in the water sample. The double bonds within the aromatic rings absorb UV light at this wavelength. The SUVA value is determined by dividing the UV_{254} by the DOC concentration of the sample. SUVA is an indicator of the composition of the organic carbon; it basically provides the amount of humic substances relative to non-humic substances in a water sample (Weishaar *et al*., 2003; Edzwald and Van Benschoten, 2010).

1.3.3 Bacterial degradation of NOM

According to Young (2005), bacterial degradation of intermediate to LMW NOM components cause the molecular weight (M_w) of NOM in solution to increase. Results of this study have also indicated that NOM bioavailability is not solely dominated by molecular weight and other factors in conjunction with microbial community structure have an effect on bioavailability. Various studies have also suggested that the LMW organic matter fraction is more biologically reactive (i.e. more rapidly utilised) and produces higher bacterial yields than

HMW dissolved organic matter (Axmanová *et al*., 2006; Khodse & Bhosle, 2011). The LMW and HPI NOM fractions are the NOM components that are not easily removed by conventional water treatment (Van Leeuwen *et al*., 2005) and are more prone to DBPs formation if they remain in the post-treatment water (Hwang *et al*., 1999, Marhaba & Van, 2000). Albeit time consuming (6 days), the BDOC method used by Nkambule *et al*. (2011) as a NOM characterization tool measures the availability of NOM to be utilised by bacteria.

Within this thesis the focus will be on providing an additional NOM characterization tool by using this BDOC method as a foundation. The aim of this altered BDOC technique is to specifically incorporate the bacterial degradation of the individual NOM fractions and provide a more rapid technique for characterization of the problematic fraction. It was envisioned that this altered technique would provide a better understanding of how the chemical composition of NOM (specifically the polarity) affects bioavailability and thus give an insight into the relationship between polar NOM fractions and bacterial utilisation.

1.3.4 Effects of NOM on chlorinated DBPs

In 1974 J.J. Rook reported that insufficient removal of NOM from surface water during potable water production can produce DBPs when residual NOM reacts with chlorine during the disinfection process (Howe *et al*., 2012). The DBPs of most concern due to their elevated amounts and prevalence in chlorinated water are trihalomethanes (THMs) and haloacetic acids (HAAs) (Frimmel & Jahnel, 2003; Kristiana *et al*., 2011). Although chlorinated/chloraminated water generally has lower THM and HAA concentrations than chlorinated waters (Knight *et al*., 2011), they pose a risk of forming an additional by-product of significant health concern called N-nitrosodimethylamine (NDMA) (Mitch *et al*., 2003; Howe *et al*., 2012).

Considerable research efforts have recently been directed towards determining the effect of NOM character based on molecular weight (Chowdhury, 2013; Özdemır, 2014) and polarity (Lu *et al*., 2009; Roe *et al*., 2008; Tubić *et al*., 2013) on DBP formation. It is well known that certain NOM fractions can elevate the amount of DBPs formed (Marhaba *et al*., 2003) and also result in the formation of specific chlorinated by-products (Özdemır, 2014). To this end, the amount of DBPs formed is known to be affected by various properties associated with the organic precursors (Chang *et al*., 2001).

1.3.5 NOM treatability during potable water treatment

In this work, the treatability of NOM from the Vaal Dam surface water that is currently utilised by Rand Water for potable water treatment is investigated. To achieve this goal, various NOM characterization techniques were utilised to determine the composition and character of NOM within the source water and during the water treatment processes (i.e. coagulation/flocculation, sedimentation and sand filtration). Once the individual NOM fractions that were removed by the individual treatment units of the full scale plant were identified, a DBP formation potential assessment was undertaken with the aim of determining the specific DBPs that were formed from these individual NOM fractions. A biodegradability study of the individual NOM fractions using the modified BDOC method was also carried out.

Other than identifying the residual NOM fractions that are not removed during potable water treatment, it was envisioned that these characterization techniques would enable the amount of carbon available to sustain microbial growth to be determined as well as allow the NOM fractions that increase heterotrophic bacterial growth to be determined. Upon completion of this part of the work, a water treatment technology that enhances the removal of the problematic NOM fractions and can be used as an additional step in the current conventional water treatment process will be proposed. In order to allow proper monitoring of NOM composition in the source water that will contribute towards the enhancement of NOM removal by the full scale conventional treatment plant, a routine NOM characterization and monitoring protocol that employs specific NOM characterization techniques will also be proposed.

1.4 OBJECTIVES OF THE STUDY

This research study is aimed at recommending a NOM characterization protocol to be utilised by drinking water treatment practitioners and laboratory personnel. Specifically, the protocol will be used for:

a) routine monitoring of NOM removal during water treatment;
b) providing insight into the prediction of NOM removal and DBP formation within the treatment process; and

c) identifying the specific NOM fraction that is not effectively removed by the water treatment plant, determining the easily biodegradable fraction and the fraction that is the main precursor to the formation of THMs.

The research questions formulated are:

i. Can a dependable NOM characterization method be developed to assess NOM in surface water that differs in both quality and quantity?
ii. Do currently employed Rand Water processes sufficiently remove NOM from its source water to prevent subsequent DBP formation in the final drinking water?
iii. Will a reduction of biodegradable dissolved organic carbon (BDOC) as well as the hydrophilic NOM fraction result in decreased DBP precursor and NOM removal rate since the hydrophilic NOM fraction (having lower SUVA values) is currently not removed by the Rand Water's treatment process?

In order to address the formulated research question, the following key objectives were set:

i. Use FEEM, m-PRAM, HPSEC, UV_{254} and SUVA techniques to characterize NOM and determine its composition in the Vaal Dam surface water as well as in the final drinking water produced by Rand Water.
ii. Investigate the effect of NOM polarity and aromaticity on the formation of DBPs by isolating the HPO, HPI and TPI NOM fractions and subjecting them to chlorination to produce the 'desired' THMs for each NOM fraction.
iii. Identify seasonal trends between hydrophilic and hydrophobic NOM fractions within the source water as well as the formation of THMs after chlorination in order to permit the optimisation for the removal of the problematic NOM fractions.
iv. Optimise the BDOC method (fundamentally making use of bacteria on filter sand as inoculum and using the initial and final DOC value over a time to calculate the BDOC measurements) by first coupling the biodegradable organic matter to the three NOM fractions isolated by the m-PRAM fractionation procedure.
v. Address current characterization needs in potable water treatment by providing a protocol to follow for NOM characterization and routine monitoring of NOM removal.

1.5 THESIS OUTLINE

The remainder of this thesis is structured as follows:

Chapter 2 – Literature Review: The fate of NOM within the water industry, treatability of NOM during potable water treatment and challenges associated with currently available NOM characterization techniques are discussed in this chapter.
Chapter 3 – Experimental Methodology: All experimental and analytical methods utilised in order to achieve the objectives of this study are outlined in Chapter 3.

Chapter 4 – Investigating the character of natural organic matter (NOM) and its removal by full scale conventional water treatment: This chapter is presented in a form of an already published paper, *Water Science and Technology; Water Supply*, Volume 17.5 (2017) 1287-1397. This chapter demonstrates the variability in NOM character in the Vaal Dam surface water, the change in NOM polarity and seasonal NOM removal during the study period.

Chapter 5 – Relationship between the character of NOM fractions and the formation of trihalomethanes (THMs): This chapter presents work based on the effect that NOM character has on the distribution of THMs formed. Specifically, the effect of NOM character (using specific ultraviolet absorbance (SUVA) and molecular size distribution) on the formation of THMs after chlorination and chloramination during various seasons of the year is presented. Correlating the molecular size of NOM within the source water against the actual THM formation in the final water is also reported.

Chapter 6 – Innovative and enhanced techniques to characterize fractionated THM precursor material: This chapter is focussed on the use of improved innovative techniques namely modifed-PRAM and enhanced-BDOC method, for the determination of the quantity and quality NOM fractions. Fluorescence was used to characterize THM precursor material.

Chapter 7 – Conclusion and Perspectives: The conclusion, perspectives and recommendations for future work is presented in Chapter 7.

References – All references used in each chapter are listed at the end of that chapter.

Appendix – Supplementary tables and figures of results are presented in this section.

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CHAPTER 2: LITERATURE REVIEW

This chapter reveals the importance of being familiar with the character of natural organic matter (NOM) in drinking water systems. Furthermore, it highlights the need to address NOM as a precursor to disinfection by-product (DBP) formation in final drinking water. This review motivates the need to characterize and monitor NOM during potable water treatment in South Africa.

2.1 INTRODUCTION

The most significant fate of NOM is the role NOM plays during water treatment when providing safe water to the public. There is a sound understanding that is abundantly documented indicating that NOM reacts with chlorine during disinfection of water treatment to form DBPs such as trihalomethanes (THMs), which end up in the final drinking water (Rook, 1974; Kitis *et al*., 2002; Kristiana *et al*., 2011; Golea *et al*., 2017). It is therefore imperative to effectively remove NOM to combat these water quality and operational problems during potable water treatment. It is desirable to determine the composition (quantity and quality) of the NOM present in a water source as this will enable the establishment of the most suitable treatment regime for the reduction of NOM and the subsequent formation of DBP in the water source.

2.2 CLASSIFICATION OF NOM

2.2.1 Origin of NOM and its classification

NOM has an intrinsic chemical composition and is a varying-compound mixture that is globally present in all water sources (ground-, surface- and natural waters). Partly decayed organic substances from animal or plant material within the water body or compounds that filter from the terrestrial environment into the surface water due to rainfall, are the primary contributors of NOM.

The various NOM groupings and terminology associated with organic matter are classified and depicted in a non-complicated way in the basic Venn diagram shown in **Figure 2-1** (Pagano *et al*., 2014). According to **Figure 2-1**, the entire organic pool that occurs in natural

water sources, which is known as total organic matter (TOM), is comprised mainly of dissolved organic matter (DOM), an undissolved organic matter fraction, dissolved organic nitrogen (DON) and dissolved organic phosphorous (DOP). In surface water, humic substance consists 50 to 70% of the DOM concentration (Thurman, 1985). The major fraction of NOM is known as DOM (Penru *et al*., 2005; Pagano *et al*., 2014). The dissolved organic carbon (DOC) concentration within different aqueous environments varies considerably as a function of forest type. In addition, leached water will greatly differ and impact the carbon loading from these environments (Gough *et al*., 2012). NOM concentration varies substantially throughout the world due to various origins of DOC; NOM originating from algal sources generally have a large nitrogen fragment, low aromatic carbon and a phenolic composites.

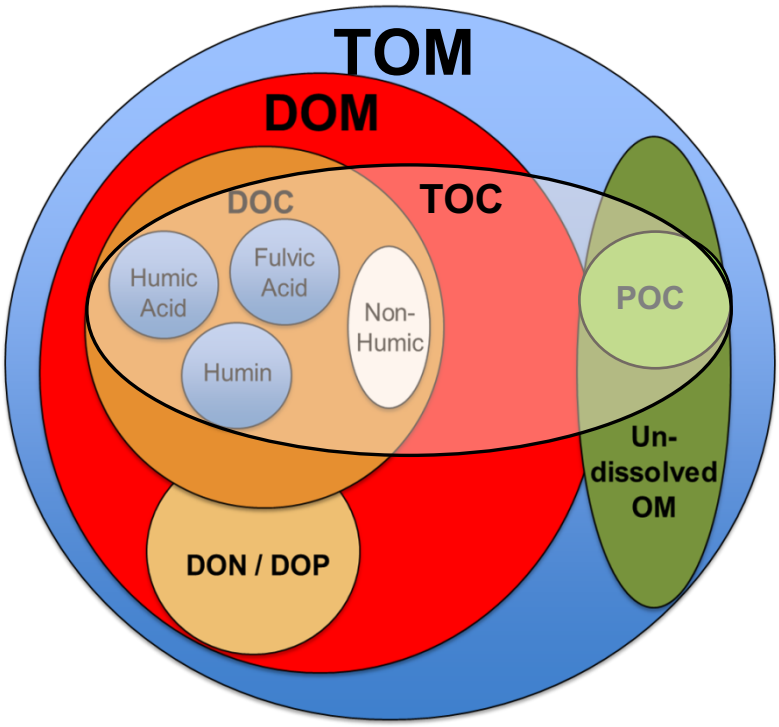

Figure 2-1: Representation of total organic matter (TOM) in the environment (Pagano *et al*., 2014)

NOM is often referred to as DOC, the constituents in solution that pass through a 0.45 µm filter paper, with particulate organic carbon (POC) being the fraction that remains on the filter after establishing the total organic carbon (TOC) (Kitis *et al*., 2001). **Figure 2-2** shows the size range of the dissolved and particulate organic matter, with the organic carbon being smaller than 0.45 µm and the fulvic acids being about 2 nm in diameter (Thurman, 1985).

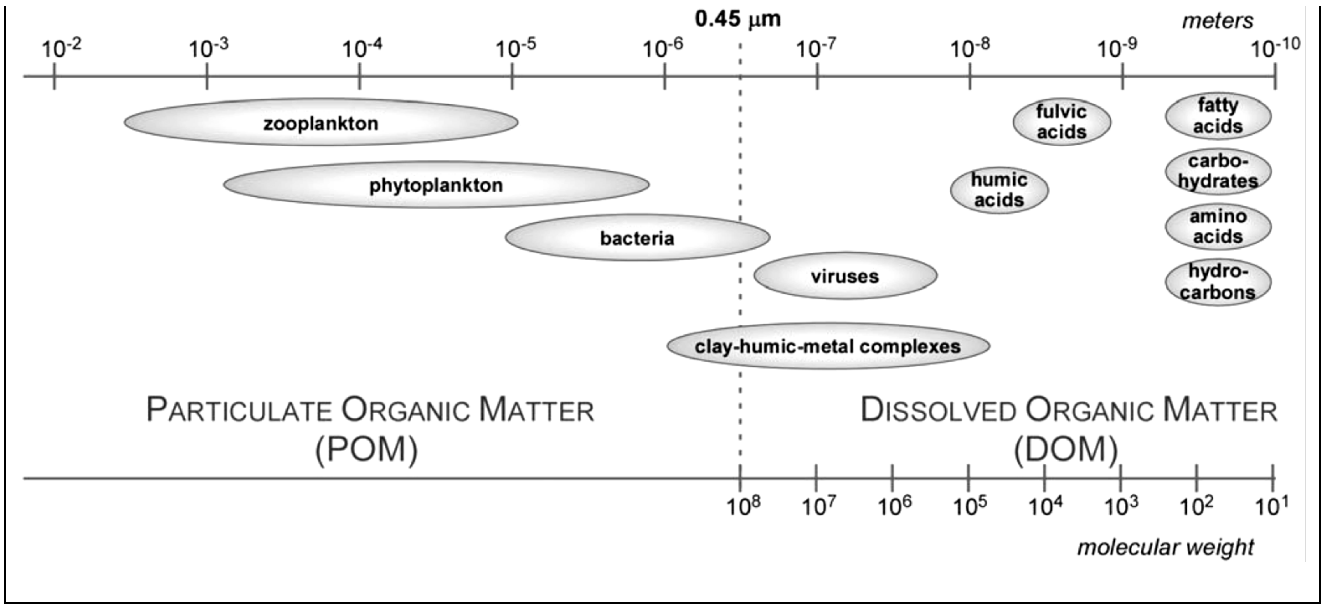

Figure 2-2: Size range of DOM and POM **(Docter *et al*., 2015)**

Surface water DOC mainly comprises of humic and non-humic components, with humic substances being divided into humic acid, fulvic acid and humin (Pagano *et al.,* 2014). As indicated in **Figure 2-3**, NOM fractionation techniques are able to separate DOM into transphilic (TPI), hydrophilic (HPI) and hydrophobic (HPO) fractions. Based on molecular size and polarity, humic components are hydrophobic (HPO) and non-humic components are hydrophilic (HPI) in nature (Edzwald & Tobiason, 2010). Based on the chemical properties of NOM fractions, other examples of HPO NOM include humic acids, fulvic acids, hydrocarbons, phenolic hydroxyl groups, aromatic rings or conjugated double bonds (Leenheer & Croué, 2003; Garcia, 2011). HPI NOM includes compounds such as aliphatic ketones and alcohols (Thurman, 1985; Świetlik *et al*., 2004). A summary of the classification and chemical composition of NOM fractions is shown in **Figure 2-3**.

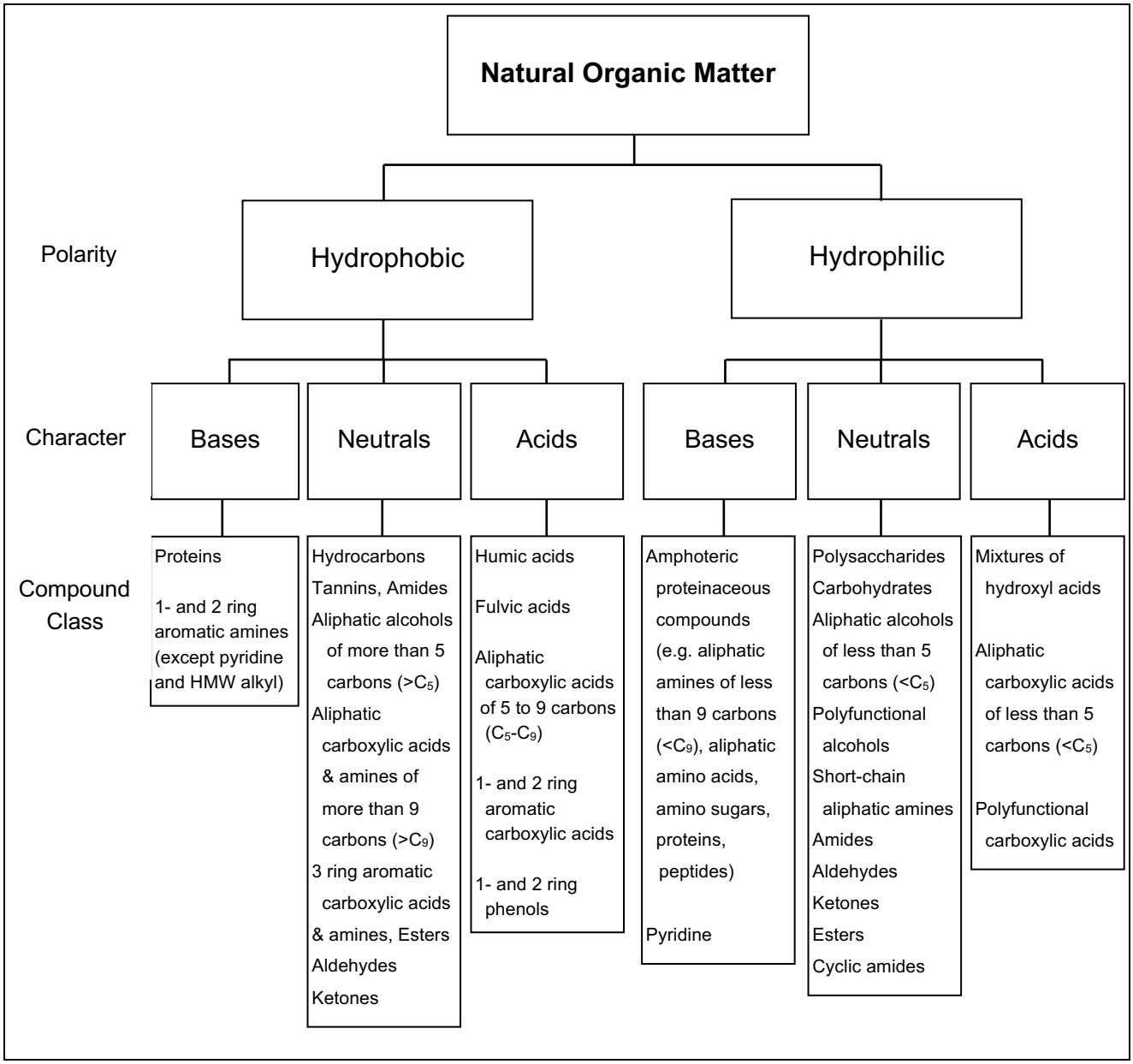

Figure 2-3: Classification and chemical composition of NOM (adapted from Leenheer *et al*., 2003, Świetlik *et al*., 2004)

2.3 THE IMPACT OF NOM ON POTABLE WATER SYSTEMS

2.3.1 Seasonal variability of NOM

Although the seasonal variability of NOM composition and concentration is not well established, some trends in DOC loading and NOM quantity have been reported in diverse environments. For example, an increase in the concentration of HPI DOC has been linked to temperature changes (Kaizer *et al*., 2001). Changes in the fluorescence and ultraviolet

absorbance (UV) of organic carbon as well as increases in the concentration of DOC following periods of heavy rainfall have been documented (Krasner *et al*., 1996).

Although an increase in the values of the ultraviolet absorbance at 254 nm (UV_{254}) occurred during winter and spring (January to May), very little seasonal variation in the concentration of the organic matter was observed in the source water during the same period (Matilainen *et al*., 2002). Although high HPSEC values were detected during spring, the lower values that were observed during summer slowly increased at the onset of winter (Matilainen *et al*., 2002). Studies by Szabó & Tuhkanen (2007) also confirmed the patterns of molecular weight seasonality; an increased amount of HMW organics were evident during winter and spring and a low concentration of the HMW fraction was observed in summer.

In contrast, TOC levels did not follow a similar trend; very low TOC concentrations that were detected during winter months increased to between 5.1 and 6.3 mg/L towards the summer months. The increase in DOC could possibly be due to algal growth or decreased discharge from the neighbouring environment (Thurman, 1985). This increased organic carbon loading, which is measured as DOC, also resulted in high THM formation during the summer months (Knight *et al*., 2011). Compared to summer months, as much as four times the levels of DOC were observed in source water samples during winter and spring months (Szabó & Tuhkanen, 2007). Although the DOC levels were high, the increased NOM was problematic to the water treatment plant (WTP) as organic matter could not be adequately removed due to low temperatures.These low temperatures during the winter and spring months negatively influences the floatation and filtration treatment steps at the specific WTP (Szabó & Tuhkanen, 2007). In contrast, Bazrafshan *et al*. (2012) has found that the NOM concentration levels did not follow a specific seasonal trend.

The characterization and monitoring of the quantity and quality NOM within a specific water source could be of great benefit to WTPs as suggested by Gough *et al*. (2012). Seasonal variability in the composition and concentration levels of DOC will enable plant operating personnel to consider alternative or additional treatment options when irregular NOM levels are expected in the raw water source.

2.3.2 Water quality concerns and operational interferences

Other than producing decreased water quality, substandard removal of NOM during potable water treatment also creates operational problems at the WTPs and the water distribution

system. Not only is NOM the culprit behind undesirable taste, odour and colour divergences in the final drinking water, the biodegradable organic carbon fraction of NOM stimulates bacterial growth within the water distribution systems (LeChavelier, 1991; Van der Kooij, 1992). Lastly, research has confirmed that HPI NOM tends to be the main precursor to the regrowth of bacteria within the pipe distribution system (Świetlik and Sikorska, 2006; Matilainen and Silanpää, 2010). Nonetheless, the major concern with inadequate removal of NOM is the formation of disinfection by-products (DBPs), which is brought about by the reaction of NOM with the oxidant during the disinfection step. It is noteworthy that such DBPs, which are typically harmful to humans, animals and the acquatic environment, end up in the final drinking water. It suffices to say that increased chlorine demand as well as high DBP formation following the disinfection process is generaly linked to high NOM concentrations within source water (Edzwald & Tobiason, 2010).

2.3.3 Disinfection by-product (DBP) formation

Well over 600 DBPs formed using various disinfectant strategies have been detected in final drinking water (Richardson *et al*., 2007). The aim of NOM research is often to compare NOM characteristics and its influence on the treatability and DBP formation during the disinfection step with the ultimate objective of optimising NOM removal technology (Gough *et al*., 2012). Within the potable water supply industry, it is mostly the halogenated DBPs (THMs and HAAs) that are regulated due to their frequent occurrence in final drinking water (USEPA, 2006; Health Canada, 2008; WHO, 2011; SANS 241, 2015). The regulatory limits of HAAs and THMs set by the United States Environmental Protection Agency (USEPA) are 60 µg/L and 80 µg/L, respectively. According to the World Health Organization (WHO), the limit for THMs is 100 ug/L. In South Africa, the four THMs, namely bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform and chloroform are individually regulated with no drinking water standard regulating HAAs (SANS, 2015). As shown in **Table 2-1**, not only have high concentrations of THMs and HAAs been detected in final drinking water, other DBPs such as halonitromethanes (HNMs), haloketones, haloacetonitriles (HANs) and haloaldehyde have also been detected in significant amounts (Bond *et al*., 2012). Additional DBPs (e.g. iodo-THMs) that are not regulated have also been detected in drinking water.

Table 2-1: Significant DBP classes (Bond *et al*., 2012)

Class	Structure	Important DBPs
Trihalomethanes (THMs)		Chloroform ($CHCl_3$) Bromoform ($CHBr_3$)
		

012)

2.3.3.1 Effect of bromide and iodide

It has been demonstrated that bromine is much more reactive towards low molecular weight (LMW) organics than high molecular weight (HMW) NOM (Chowdhury, 2013). Further evidence was provided by a study conducted by Kitis *et al*. (2002), which demonstrated a higher incorporation of bromine into the non-aromatic LMW HPI NOM components. According to this study, the HPI fractions also contained higher concentrations

of brominated species within haloacetic acids (HAA) and trihalomethanes (THM) (Kitis *et al*., 2002).

The presence of bromine in environmental water increases the potential to form brominated DBPs as bromine affects the distribution of the DBP species (Kristiana *et al*., 2010; Knight *et al*., 2011; Ramavandi *et al*., 2015). A decrease in the pH during water treatment process could result in a reduction in the formation of chloroform. However, at elevated pH, water containing high bromide ions leads to an increase in the concentration of brominated THMs (Chowdhury, 2013). According to Zhang *et al*. (2016), increased iodide concentration (and NOM concentration) resulted in large I-THM formation primarily from the LMW NOM precursors.

As indicated by Le Roux *et al*. (2012), although inorganic constituents (bromide and iodide) greatly influences the formation of specific classes of DBPs (e.g. bromide enhances N-nitrosodimethylamine (NDMA) formation), the major contributor to DBP formation is NOM (Kristiana *et al*., 2010; Lin *et al*., 2014).

2.3.3.2 NOM fractions as DBP precursor

Not all organic compounds react the same with a disinfectant to form DBPs since the NOM character (molecular weight, hydrophobicity) affect the distribution and spatial variability of THMs (Liang & Singer, 2003; Zhang *et al*., 2016; Li *et al*., 2017). The main classes of DBPs present in drinking water that are formed following the disinfection process are HAAs and THMs (Frimmel & Jahnel, 2003; Bond *et al*., 2009).

Save for pH, temperature and chlorine concentration, DBP formation is also influenced by the presence of high or low MW NOM (Lin *et al*., 2014). The molecular weight of organic matter influences the formation of I-THM during chlorination and chloramination (Zhang *et al*., 2016). HMW NOM (> 100 kDa) formed higher amounts of I-THMs compared to LMW during the chlorination step, whereas a high pH resulted in the formation of high amounts of I-THM from the LMW fraction. For HMW fractions, the levels of I-THM decreased with increasing NOM concentration during the chloramination step. In a study conducted by Lin *et al*. (2014), DBP formation caused by iodine was mostly due to the presence of the organic components within the HPI fraction. Zhang *et al*. (2016) also documented that the concentration of I-THM decreased with increasing pH for all molecular weight fractions (both

LMW and HMW). Therefore, HMW NOM has the propensity to generate higher levels of I-THM compared to LMW during chlorination and chloramination steps.

It has also been demonstrated by Kristiana *et al*. (2010) that larger amounts of brominated DBPs occur when the aromaticity and molecular size of organic matter decrease. According to Chowdhury (2013), brominated THMs increase when the molecular weight of the organic matter decrease. This is evidenced by the fact that on average the HMW NOM produced 40% less bromodichloromethane (BDCM) and dibromochloromethane (DBCM) compared to the LMW fraction with a molecular weight below 500 dalton (Da) (Chowdhury, 2013). Therefore, LMW components have a higher reactivity towards bromide ions compared to chloride ions. On the contrary, some researchers have found the LMW HPI fraction to be more prone to the formation of THMs (Zhao *et al*., 2006; Özdemir, 2014).

When investigating the influence of the molecular size of NOM on the formation of THM, Zhang *et al*. (2016) also found that the molecular weight plays a vital role because HMW compounds produced more iodated-THMs compared to the LMW NOM fraction. When comparing HPO HMW NOM (> 0.5 kDa) to LMW HPI NOM, the aromatic NOM having a larger molecular weight was the precursor for total organic halogen DBP formation during chlorination and chloramination. A correlation between HMW organic matter and the individual THM species has been reported in other studies (Chowdhury, 2013; Zhang *et al*., 2016), which indicate that HMW NOM is more reactive towards chlorine. Chloroform formation reportedly increased with increasing molecular weight to an extent that HMW produced 67-75% more chloroform compared to when NOM of LMW was used as the precursor (Chowdhury, 2013).

Various researchers have investigated the distribution of the different NOM fractions and their mass contribution (measured as DOC) in relation to the DBPs formed (Gough *et al*., 2012; Chowdhury, 2014; Pifer & Fairey, 2014). HPO NOM is the key contributor to the formation of THMs (Hua & Reckhow, 2007), and the formation of NDMA appears to be largely formed due to the presence of HPI and TPI organic matter fractions (Chuang *et al*., 2013). Li *et al*. (2017) concluded that HPO NOM was the major precursors to nitrogenous THM and the HPI fraction is likely to form more ketones. THM (specifically chloroform) formation increases due to the presence of HMW organics at elevated pH values, whereas brominated THMs (BDCM, DBCM, bromoform) decrease with increased pH and HMW fractions.

In conclusion, the main reactive precursor within organic matter is the aromatic HMW fraction of NOM, which varies within different water sources (Gough *et al*., 2012).

2.3.3.3 Role of NOM parameters and DBP formation

Several studies have embarked on investigating the formation potential (FP) of DBP using surrogate NOM parameters (e.g. SUVA, UV_{254}, DOC), hydrophobicity or molecular size) in order to:

i.) Gain a better understanding of these precursors by characterizing NOM derived from different water sources. This is because NOM character varies with respect to composition and calender seasons and regional geographical locations (Szabó & Tuhkanen, 2007; Kristiana *et al*., 2010; Nkambule, 2012).

ii.) Identify a parameter that can be applied to source waters in order to forecast the reactivity of individual NOM fractions to form THMs, (Roccaro & Vagliasindi, 2009; Matilainen *et al*., 2011; Chowdhury, 2013).

iii.) Determine the relationship between NOM character and treatability of the individual NOM fractions within source waters (Parsons *et al*., 2004; Bond et al., 2012).

iv.) Ultimately augment WTP efficiency to reduce NOM as the major precursor to DBP formation (Matilainen *et al*., 2011).

A trend that relates DBP formation to increasing SUVA values is widely recognised in the water industry due to the strong reactivity between highly aromatic compounds and chlorine (Gallard & Von Gunten, 2002; Roccaro & Vagliasindi, 2009). Source waters with bigger specific ultraviolet absorbance (SUVA) values require a larger chlorine dosage and the subsequent formation of THMs will also be higher (Abdullah *et al*., 2009). According to Edzwald & Tobiason (2010), SUVA and total trihalomethane formation potential (TTHMFP) values are closely related; SUVA values higher than 4 L/mg.m indicate the presence of HPO organic matter. On the contrary, opposing interactions have been identified where the data obtained indicate a weak correlation between SUVA and THM during the chlorination process (R^2 = 0.50) and after the chloramination process (R^2 = 0.20) (Hua *et al*., 2015).

Other NOM characterization studies have also reported a weak correlation between TTHMFP and SUVA, specifically when the raw water SUVA values were below 3 L/mg.m

(Parsons *et al*., 2004). An analysis of results from differing source waters has also revealed a weak correlation between TTHMFP and SUVA values (Fram *et al*., 1999; Weishaar, 2003; Wei *et al*., 2008). Nonetheless, Golea *et al*. (2017) investigated TTHMFP with SUVA, UV_{254} and HPO NOM within 30 conventional WTPs in the geographical region of Scotland and concluded that THMs correlated well to UV_{254} (R^2 correlation coefficient ranged between 0.79 and 0.82).

It can therefore be concluded that SUVA is an appropriate and suitable surrogate for the prediction of TTHMFP (Golea *et al*., 2017) and a good indicator of unknown DBPs, which is evidenced by a strong correlation between SUVA and unidentified total organic halides (UTOX) (R^2 = 0.79) (Hua *et al*., 2015). This shows that ultraviolet absorbing NOM constituents and HPO organic matter are precursors for unknown DBPs (Hua *et al*., 2015).

2.3.4 Reactivity of NOM fractions with disinfectants / Impact of disinfection on NOM

Disinfectants are commonly used to inactivate bacteria and to ensure safe drinking water to the public by employing ozone (O_3), chlorine dioxide (ClO_2), chlorine (Cl_2) or chloramine (NH_2Cl) (Viesmann & Hammer, 1998; Van der Walt *et al*., 2009). As DBP drinking water standards are becoming more stringent, WTPs are reviewing their disinfectant control strategies by researching methods aimed at decreasing the main precursor of the by-products formed at their respective WTPs. In the Sections that follow, some of the common disinfectants mentioned above are discussed in more detail.

2.3.4.1 Chlorination

Chlorine, the most common chemical used for disinfection, has been used as an effective disinfectant since 1908 at the Jersey City Water Company and Bubbly Creek (Chicago, USA) (Viesmann & Hammer, 1998; Van der Walt *et al*., 2009). Chlorine is the preferred disinfectant in the potable water industry due to its low procurement costs. Most importantly; chlorine ensures a good disinfectant residual within the distribution system. Chlorine leads to increased amounts of THMs, HAAs and TOX when compared with the utilization of other disinfectants such as chloramine or chlorine dioxide (Hua & Reckhow, 2007).

According to Li *et al*. (2017), chlorine is more likely to react with the humic-like matter in both the HPO and HPI fraction, with the protein-like materials in these two fractions, and with the fulvic acid-like components in the HPI fraction. Zhang *et al*. (2009) has also proven that

humic acids display higher reactivity towards chlorine thus producing more total organic halides (TOX) and regulated DBPs compared to fulvic acids (Li *et al*., 2017).

HPO components are more reactive towards chlorine and are the main precursor for DBPs within the ester-, alcohol- and heterocyclic-DBP chemical classes (Kitis *et al*., 2002; Li *et al*., 2017). More halogenated DBPs are generated during both chlorination and chloramination by the HPO fraction compared to HPI organics, due to the reactivity between the disinfectant and humic substances within the HPO NOM (Li *et al*., 2017).

2.3.4.2 Chloramination

In addition to chlorine, chloramine is also being more frequently used and it leads mainly to the formation of a possible health hazardous by-product called N-nitrosodimethylamine (NDMA) (Choi *et al*., 2002; Mitch *et al*., 2003; Howe *et al*., 2012; Chuang *et al*., 2013). During chloramination, the HPO fraction has been identified as the likely most the precursor for nitrogenous DBP formation (Li *et al*., 2017). According to Li *et al*. (2017), chloramine reacts with the humic-like materials and protein-like components in both the HPI and HPO fractions, and equal quantities of hydrocarbons, esters and heterocyclic DBPs are formed from these fractions. However, more ketones are formed from the HPI fraction compared to the HPO fraction (Li *et al*., 2017).

An advantage of chloramination is that it forms less THMs and HAAs (Seidel *et al*., 2005; Knight *et al*., 2011) and the amount of halo acetonitrile (HAN) formed during the chloramination process has been found to be a tenth of the the amount of THM and HAA formed (Chuang *et al*., 2013). When compared with chlorination, Li *et al*. (2017) observed that the HPI fraction forms 5-15 times more ketone DBPs during chloramination and ozonation, and that smaller concentration of the other classes of DBPs are formed during chloramination. Zhang *et al*., 2007 found that iodo-trihalomethane (I-THM) formation from the HMW fraction decreased during chloramination. Oxidation preceding chloramination is an effective control measure to limit NDMA formation (Bond *et al*., 2011).

2.3.4.3 Chlorine dioxide (ClO_2)

Other than having a strong bactericidal effect over a wide pH range, the most important advantage of ClO_2 is that it does not react with nitrogenous and humic components to form chloramine and trihalomethanes, respectively (Viesmann & Hammer, 1998). Chlorine

dioxide results in smaller THM and HAA formation when compared with the use of chlorine as a disinfectant (Chang *et al*., 2001). It is evident from a study by Świetlik *et al*. (2004) that components consisting of HMW character are more reactive towards ClO_2 since substantial molecular size changes were observed owing to the transformation of these molecules into smaller molecules. The reaction of HPO- and HPI-neutrals with ClO_2 forms mainly the oxidation by-products known as aldehydes and carboxylic acids (Raczyk-Stanislawaik *et al.*, 2003; Świetlik *et al*., 2004). According to Świetlik *et al*. (2004), the dominant oxidation by-products that were identified are aldehydes (i.e. acetaldehyde, formaldehyde and glyoxal), with carboxylic acids such as oxalic-, acetic and formic acids also being generated.

2.3.4.4 Ozonation (O_3)

Ozone reacts with humic matter and DBP precursors are reduced by removing the aromatic components as indicated by a reduction in UV_{254} values after ozonation (Gallard & Von Gunten, 2002; Tubíc *et al*., 2003, Plourde *et al*., 2015). During ozonation double the amount of DBPs is produced due to the HPI fraction compared to the HPO fraction, although the HPO fraction appears to be a heterocyclic DBP precursor (Li *et al*., 2017). Nonetheless, ozonation is able to remove 50-60% HPO fractions, which act as N-nitrosamine precursors. In addition, the HPI fraction is increased possibly from the transformation of the HPO components into HPI precursors (Liao *et al*., 2015).

Although pre-ozonation is not very successful in reducing the chlorine demand of water, up to 75% of THMs formed can be removed due to reactivity of ozone and dihydroxybenzenes and carbonyl compounds (Gallard & Von Gunten, 2002). According to Hua & Reckhow (2007), pre-ozonation showed the ability to decrease the formation of UTOX from post-chlorination. It should also be noted that an increase in the generation of UTOX was detected following pre-ozonation of source water having low humic matter. The reaction of ozone with HPI bases, HPI neutrals and the humic acid (HA) fraction were the major contributors to the formation of biodegradable aldehydes, as documented by Świetlik *et al*. (2004).

A study by Singer *et al*. (2003), which involves the intermediate ozonation (IO_3) disinfection after the coagulation and settling steps, concluded that IO_3 is highly influenced by source water characteristics. IO_3 was found to reduce the TTHM and HAA concentrations by 10-44% and 6-61%, respectively. However, the chlorine reactivity increased slightly compared to the use of alum coagulation without ozonation (Plourde *et al*., 2015).

2.4 NOM QUANTITY AND QUALITY: FRACTIONATION AND CHARACTERIZATION

2.4.1 Introduction

Fractionation of organic matter entails separating organic molecules with similar chemical properties (e.g. molecular size, polarity and fluorescence) and then identifying them through elemental composition analysis in order to assess the impact that the specific fractions have on the DBPs formed (Matilainen *et al*., 2011). Organic matter fractionation provides key information on the composition and treatability of a water source, which is of great importance as variability in NOM character and organic loading might occur (Krasner *et al*., 1996; Matilainen *et al*., 2002; Parsons *et al*., 2004). The character and quantity of organic matter influences the efficacy of the water treatment process, as increased NOM removal are expected when aromaticity or DOC concentration in the source water are high. It is of great importance that reproducible fractionation and characterization techniques are utilised instead of merely focussing on the chemical structure of organic matter (Matilainen *et al*., 2011).

2.4.2 Predicament with NOM characterization

Currently, a singular and all inclusive NOM characterization technique that can be applied on any type of source water does not exist. Nevertheless, NOM characterization techniques are globally and extensively being studied and the difficulty with NOM quantification and characterization is mostly attributed by the following aspects:

i.) Seasonality in NOM character and structure are evident (Sharp *et al.,* 2006).
ii.) Composition and character of NOM fluctuates within different geographical areas and are often site specific, thus influencing NOM treatment (Nkambule *et al*., 2012; Plourde *et al*., 2015).
iii.) Transformation in molecular weight distribution of NOM occurs due to bacterial activity during various seasons (Szabó & Tuhkanen, 2007; Khodse, 2011).
iv.) Due to the intrinsic, varying and non-uniform structure of NOM, numerous techniques are often required to ensure all properties are considered (Matilainen *et al*., 2011; Bond *et al*., 2012)

2.4.3 Isolation methods

It has been recognised that aromaticity, MW and functional group distribution of NOM influence the effective removal of NOM from water. NOM is isolated and fractioned into various chemical groups having similar characteristics, whereby the impact of the isolated fraction on the unintentionally formed DBPs can be investigated further. Prior to adopting the most suitable treatment option for the effective removal of NOM, it is important to first isolate and characterze the NOM present in the source water. The quantity and quality of NOM affects the selection of a treatment option since not all treatment options are able to equally remove all fractions from the source water (Sharp *et al*., 2006; Plourde *et al*., 2015).

2.4.3.1 XAD-resins

XAD-4 and XAD-8 resins were effectively used in columns for the separation of NOM into a HPI, HPO and TPI fraction (Leenheer, 1981). XAD-resins are the preferable technique for the fractionation of NOM (Thurman & Malcolm 1981; Marhaba *et al*., 2003). XAD-4 and XAD-8 resins were packed into two separate columns after purifying the resin by Soxhlet extraction. Acidified samples were passed through the XAD-8 column to remove the HPO NOM fraction prior to filtration of the effluent through the XAD-4 resin to remove the TPI organic matter. The last effluent consisted of only the HPI fraction and each column was rinsed with 0.1 N HCl and 0.1 N NaOH to elute the TPI matter from the XAD-4 column and the HPO matter from the XAD-8 resin (Leenheer, 1981). By using this method DOC is normally separated according to acidity-basicity and polarity into five components namely, hydrophilic neutrals (HPIN), hydrophilic bases (HPIB), hydrophilic acids (HPIA), hydrophobic bases (HPOB) and hydrophobic acids (HPOA).

2.4.3.2 Extraction using ultrafiltration

Various studies used a series of polyethersulfone ultrafiltration membranes to separate NOM present in a sample into different molecular size range by size exclusion (Cho *et al*., 1999). The series of membranes typically have cut-off values of 3 K, 50 K and 100 kDa, whereby each fraction that is separated into a specific molecular size can be further characterized (Lin *et al*., 2000; Chowdhury, 2013; Zhang *et al*., 2016).

2.4.4 Characterization techniques

2.4.4.1 Liquid Chromatography coupled with Organic Carbon Detector (LC-OCD)

LC-OCD entails the use of Liquid Chromatography (LC) coupled with organic carbon detection (OCD) making use of various size exclusion chromatography (SEC) columns that separate organic carbon into different molecular sized fractions while incorporating iongenic and hydrophobic character of the compounds (Uyguner & Bekbolet, 2005). Various studies have quantified NOM by LC-OCD so as to detect the percentage of the various organic species (polysaccharides, humics, building blocks, LMW compounds) present within the three NOM fractions (HPO, HPI, TPI) (Kennedy *et al*., 2005; Gericke *et al*., 2016).

LC-OCD chromatography has also been utilised to indicate the efficacy of the various water treatment steps in their reduction of organic compounds (Uyguner & Bekbolet, 2005; Gericke *et al*., 2016). Results of an LC-OCD study conducted by Kennedy *et al*. (2003) seem to indicate no rejection of the humic acids (20 000 - 1000 Da), LMW acids (<350 D) or neutral organics (<350 D) by the ultrafiltration membrane. LC-OCD has shown great value in the detection of the components responsible for fouling of the membrane (Kennedy *et al*., 2005). Furthermore, it was successfully applied to evaluate the removal of specific NOM compounds in WTPs and power plants. As a result, this technique has shown to be a vital tool for assisting plant operators in their plant optimisation endeavours (Gericke *et al*., 2016).

2.4.4.2 High Performance Size Exclusion Chromatography (HPSEC)

By making use of High Performance Liquid Chromatography (HPLC), the HPSEC technique separates molecules of various molecular sizes; molecules bigger than the gel pores are eluted first in the porous matrix of the column and smaller molecules enters the pores of the gel matrix (Pelekani *et al*., 1999; Nissinen *et al*., 2001). The HPSEC technique is an important technique widely used in NOM characterization studies by evaluating the molecular size distribution (MSD) of organic matter during the various water treatment steps (Vuorio *et al*., 1998; Świetlik *et al*., 2004; Matilainen *et al*., 2005). HPSEC can be used as a quick quantitative analytical tool, without the need to pre-treat samples (Nissinen *et al*., 2001). Valuable insight regarding the treatment efficiency relating to the removal of NOM having different molecular sizes can be achieved by assessing the MSD after each treatment step (Matilainen *et al*., 2002). The changing MSD of organic matter has proven to be a fast

and reliable method for determining the efficiency of the treatment process relating to NOM removal (Myllykangas *et al.,* 2002).

An HPLC chromatograph obtained from the HPSEC technique graphically demonstrates six humic fraction peaks, illustrating NOM molecular size ranging from high to low molecular weight that also estimates the quantity of each of the fraction (molecular size) present within a sample (Pelekani *et al*., 1999; Nissinen *et al.,* 2001). HPSEC usually elutes five to six NOM peak fractions. While peaks I - II are known as the HMW fractions, peaks III - IV represent the intermediate molecular weight fraction. Peaks V and VI illustrates the presence and quantity of LMW organic matter (Vuorio *et al*., 1998, Nissinen *et al*., 2001). According to Szabó & Tuhkanen (2007), the HMW fraction symbolises the humic and fulvic compounds from terrestrial origin while the non-humic fraction is represented by the LMW NOM.

2.4.5 Bulk NOM characterization

2.4.5.1 Dissolved Organic Carbon (DOC)

DOC is simultaneously utilised in NOM characterization studies as a quantitative technique to determine the organic carbon content and the bulk NOM in surface water. Operationally, DOC is the filtrate obtained from filtration of a sample through a 0.45 um filter paper (McDonald *et al*., 2004). DOC analysis does not provide sufficient information on the behaviour or character of NOM. It merely indicates the bulk amount of NOM present in a water source (Haarhoff *et al*., 2010; Matilainen *et al*., 2011).

2.4.5.2 Colour

The brown-yellow colour in water is often due to the presence of NOM and water having a darker colour has a high DOC content, which is often associated with the aromatic or phenolic content (Thurman, 1985; Pace & Cole, 2002; Uyguner *et al*., 2007; Worral & Burt, 2010). Chromophores within humic matter are made up of aromatic structures and double carbon bonds that mostly absorb at shorter wavelengths within the visible range (400 to 800 nm) thus resulting in the perceived brown-yellow colour. Gough *et al*. (2012) suggest that the HPOA fraction is related to increased colour (0.024 UV au). Furthermore, it has been illustrated that colour (absorbance at 400 nm) of the source water could assist in identifying

differences in the character of NOM fractions that influence the effectiveness of the coagulation process (Gough *et al*., 2012).

2.4.5.3 Ultraviolet absorbance at 254 nm (UV_{254})

Ultraviolet absorption spectroscopy measures the reduction of light as it passes through a water sample or after the light is reflected by the surface of a sample. This establishes the concentration by analysing absorbance at a specific wavelength using the Beer-Lambert Law. Ultraviolet absorbance at a 254 nm wavelength (UV_{254}) is associated with aromatic organic carbon (Chin *et al*., 1994; Korshin *et al*., 2009) indicating the quantity of aromatic organics due to the conjugated carbon double bonds (C=C) of the aromatic rings that absorb UV light at 254 nm (Edzwald & Tobiason, 2010). Although UV_{254} only indicates the amount of aromatic compounds, it is recognized as a surrogate parameter for NOM due to the strong relation between UV_{254} and DBP formation (Golea *et al*., 2017). Disinfectants and oxidants chemically reacts with compounds having C=C double bonds as such bonds are sites for donating electrons (Edzwald & Tobiason, 2010).

2.4.5.4 Specific ultraviolet absorbance (SUVA)

The method development for SUVA was undertaken by Edzwald *et al*. (1985) and SUVA indicates whether the NOM can be classified as humic matter, non-humic matter or a combination thereof. A SUVA value is calculated by dividing the UV_{254} measurement by the DOC (mg/L) concentration and multiplying by 100. Often a positive correlation between HMW and HPO substances is observed (Edzwald & Tobiason, 2010; Bazrafshan *et al*., 2012). A high SUVA value of a sample (> 4 L/mg.m) indicates high aromatic content of a sample (Edzwald & Tobiason, 2010). Bazrafshan *et al*. (2012) observed a strong positive correlation between UV_{254} and DOC (R^2 = 0.9046) and higher UV_{254} values were observed during increased DOC concentrations.

Many researchers have studied NOM fractionation and have established that surface waters with high SUVA values (< 4 L/mg.m) are comprised mainly of HMW organic matter components with an HPO character (Weishaar *et al*., 2003; Świetlik *et al*., 2005; Chowdhury, 2013; Edzwald and Van Benschoten, 2010). In a study undertaken by Chowdhury (2013), 43.8% of the DOC was recognised as HMW NOM with a molecular size greater than 1 kDa. NOM fractions having a molecular size less than 1 kDa were found to possess lower SUVA values (< 3 L.mg.m) (Özdemir, 2014).

As evidenced by a correlation coefficient of $R^2 = 0.996$ and a regression coefficient of 0.880 between SUVA and DOC, a strong positive association between DOC and UV_{254} was documented by Chowdhury (2013). However, it should be borne in mind that the LMW organic matter also contributes to the organic carbon concentration even though it is not represented by UV_{254} or SUVA.

2.4.6 Advanced NOM characterization techniques

Advanced NOM characterization techniques are different in the sense of bulk characterization methods. Advanced NOM characterization techniques do not provide information on the bulk NOM, but predominantly breaks down the multifaceted organic matter compounds into smaller components. These smaller components are categorised, having similar characteristics based on their fluorescence, polarity or molecular size.

2.4.6.1 Polarity rapid assessment method (PRAM)

By using a non-polar, polar, and anion-exchange solid phase extraction (SPE) cartridge, PRAM fractionates NOM based on polarity by separating the organic matter into HPI, HPO and TPI fractions. Ultraviolet absorbance at 254 nm (UV_{254}) is used in combination with PRAM to assess the concentration of each fraction that is adsorbed or not adsorbed onto the SPE cartridges (Rosario-Ortiz *et al*., 2004). The change in polarity of the NOM that is evaluated after each water treatment step can provide a valuable technique for evaluating the efficiency of the water treatment process with regards to the HPO, HPI or NOM fractions that has been removed by the WTP. Since PRAM gives insight into the hydrophobicity and quantity of the individual fractions, the treatability of the surface water can also be established.

Organic matter can be characterized by PRAM fractionation, by characterising NOM according to charge using NH_2, SAX cartridges, and polarity by using C18, C8, C2, CN, silica and Diol cartridges (**Table 2-2**) (Rosario-Ortiz *et al*., 2004; Rosario-Ortiz *et al*., 2007; Philibert *et al*., 2008). Liao *et al*. (2015) used PRAM to establish which component of N-nitrosamine (NA) precursors are removed during treatment (conventional WT, ozonation, bio-treatment, activated carbon) by analysing the difference between the influent and effluent of the SPE cartridge. This investigation made use of the C18 and SCX PRAM cartridges whereby the organics adsorbed onto the C18 cartridge are known as the HPO

fraction and their filtrate is the HPI fraction; on the other hand, the organic matter adsorbed onto the SCX SPE cartridge is the cation fraction (Liao *et al*., 2015). The matrices employed for the C18 and SCX cartridges are octadecyl-silyl and benzenesulforic acid-silyl, respectively.

Table 2-2: SPE cartridges for PRAM fractionation to quantify HPO, HPI and TPI NOM character

SPE cartridge	Polarity of SPE sorbent	Fraction retained
Quantify HPO character		
C18	Non-polar	hydrophobic
C8	Moderate non-polar	hydrophobic
C2	Moderate non-polar	hydrophobic
Quantify HPI character		
Silica	Polar	hydrophilic
Diol	Polar	hydrophilic
CN	Moderate polar	hydrophilic
Quantify TPI character		
NH_2	Weak anion exchange	transphilic
SAX	Strong anion exchange	transphilic

The Rosario-Ortiz PRAM was modified by Nkambule (2012) by using only three of the cartridges to elute the adsorbed material from the C18 and CN cartridge. Most importantly, the modified PRAM techniques were used as an opportunity for transforming the Rosario-Ortiz PRAM method from parallel SPE to a series PRAM thus producing a more rapid technique in the process (Nkambule, 2012). **Figure 2-4** is a graphical diagram of the modified PRAM technique whereby 0.1 M NaOH was used for the elution of the HPI and HPO fractions from the CN and C18 cartridges, respectively (Nkambule, 2012). Filtrates from the C18 and CN cartridge were passed through the NH_2 sorbent to generate an HPI fraction, which is a combination of HPO and HPI components. A comparison of the Fluorescence Excitation-emission Matrix (FEEM) spectroscopic data and the results obtained from the modified PRAM (m-PRAM) technique that utilises only three sorbents (C18, CN, NH_2) revealed that similar results pertaining to NOM composition and aromaticity were obtained (Haarhoff *et al*., 2012, Nkambule *et al*, 2012).

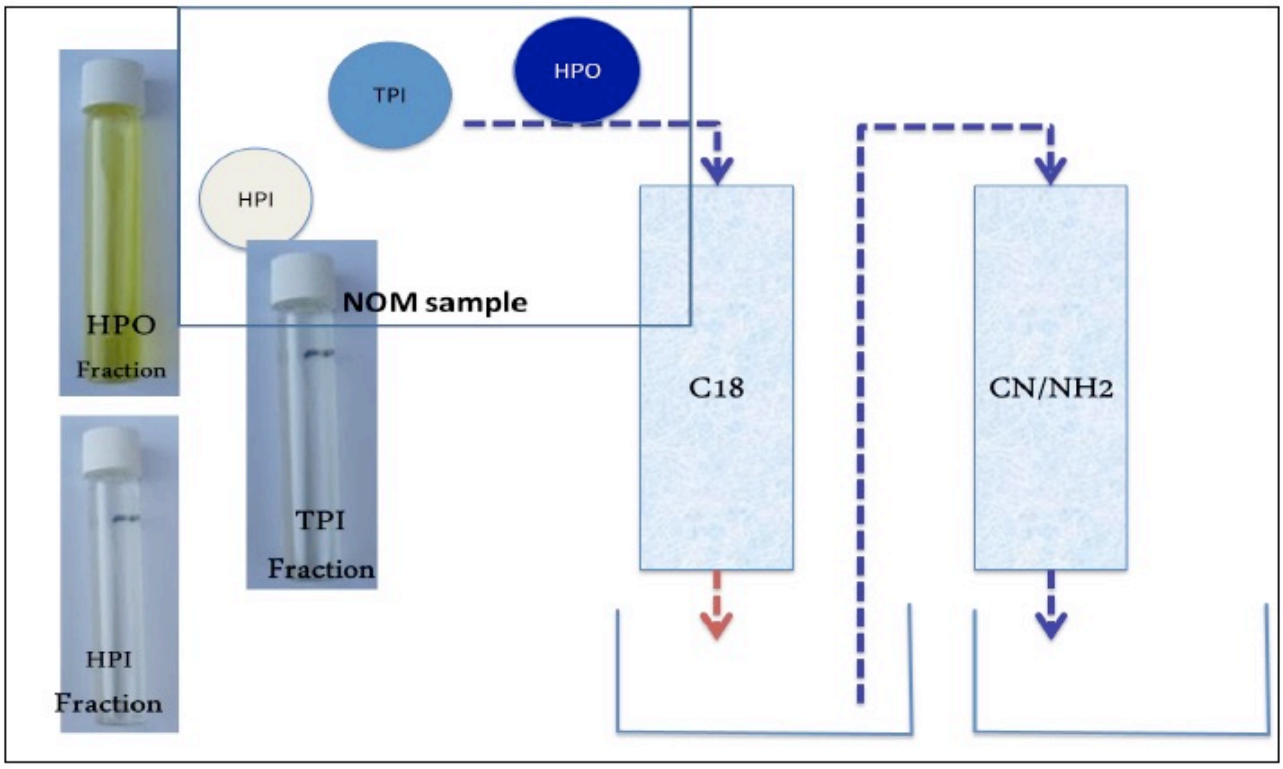

Figure 2-4: Modified PRAM (m-PRAM) to characterize NOM into a HPO, HPI and TPI fractions (Nkambule *et al*., 2012)

2.4.6.2 Fluorescence Excitation-Emission Matrix (FEEM)

Not only is fluorescence spectroscopy a beneficial and consistent technique that can be used for monitoring and assessing the character of NOM, it can also be used for determining the treatability of NOM by assessing the effect that each water treatment step has on the individual NOM components (Baghoth, 2012; Peleato, 2013). Another advantage of FEEM is that changes in the mean position of the maxima of the excitation emission wavelengths can be utilised to distinguish between humic matter originating from different sources due to humic matter that are chemically diverse in different environments (Coble,1996).

Other than establishing the source (e.g. terrestrial) of a compound, FEEM can also be used to determine the nature and concentration of organic matter. This is important since NOM concentration and chemical composition impacts on the fluorescence intensity and contours of the fluorescence spectra (Coble, 1996). According to Baghoth *et al*. (2009), excitation-emission matrix (EEM) provided evidence for impact of the protein-like or humic-like components on the treatment plant. However, it was found that the FEEM technique does not show any potential for the quantification of the actual concentration of the fluorophores (Baghoth *et al*., 2009). A typical example of a FEEM spectrum of a South African surface water source is presented in **Figure 2-5** (Engelborghs & Visser, 2014).

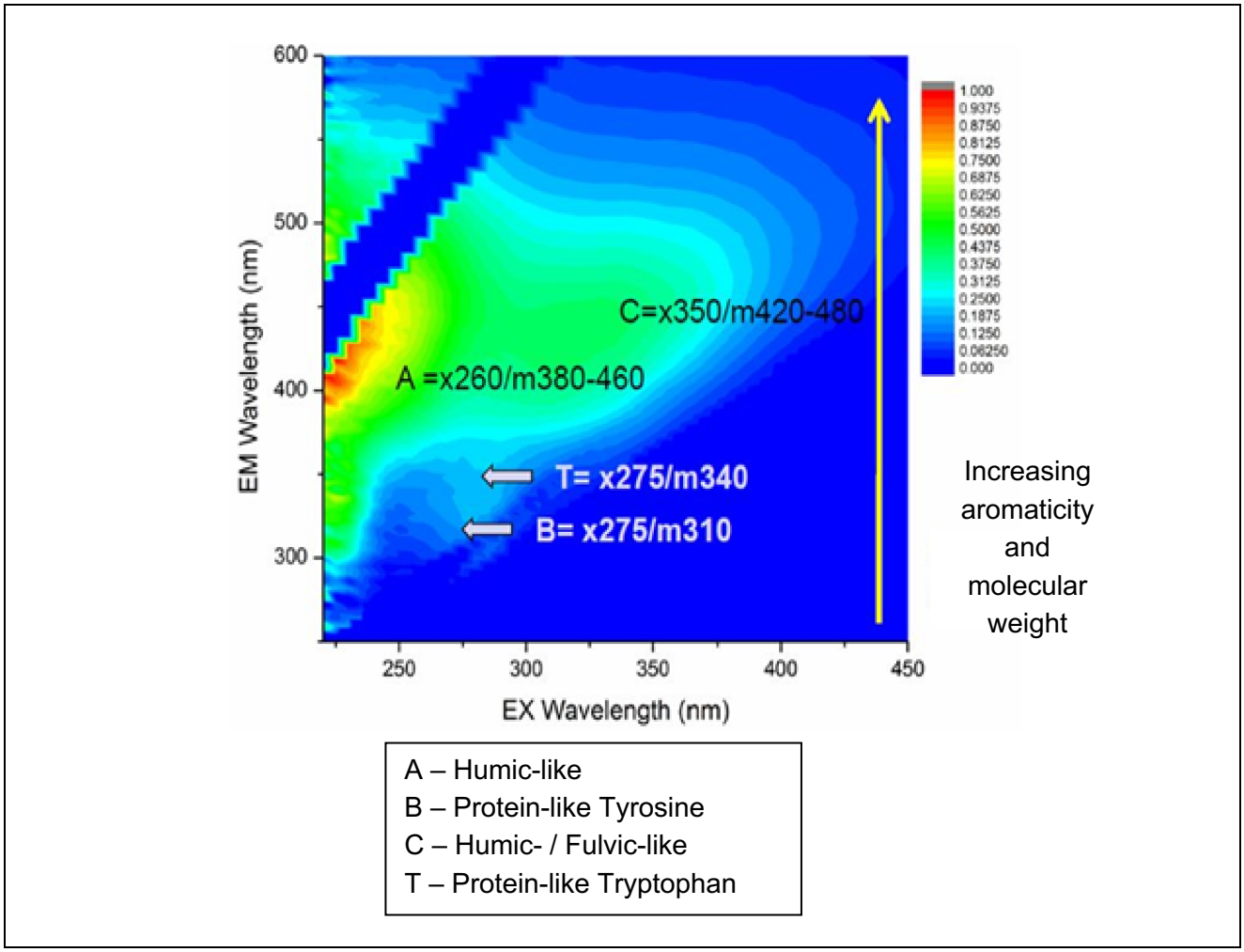

Figure 2-5: A typical surface water FEEM spectra (Engelborghs & Visser, 2014)

Coble (1996) concluded that the excitation maxima rely on the wavelength where fluorescence is detected and emission relies on the wavelength where fluorescence is stimulated. Emission scans are recorded at maximum excitation and *vice versa*, hence a fluorescence wavelength-independent position is reflected for the different fluorophores occurring in surface waters (Coble, 1996).

Results are presented as FEEM contour plots by accumulating excitation or emission spectra over a range 250 - 550 nm for surface water and and are therefore used to specify the type of organic matter existing in the sample (Coble, 1996). Fluorophores, which is known as the exact emission and excitation wavelengths of a certain molecular arrangement, is often characterized as compound groups; humic-like or protein-like. The main fluorescence intensity peaks for NOM fluorophores are indicated in **Table 2-3** (Coble *et al*., 1996; Matilainen *et al*., 2011).

Table 2-3: Fluorophores in natural water illustrating peak fluorescence positions (excitation and emission range) (Coble *et al*., 1996; Coble *et al*., 2014; Matilainen *et al*., 2011)

Peak	Excitation wavelength range (nm)	Emission wavelength range (nm)	Component description	Source
A	260	380 – 460	Humic-like	Humic Terrestrial Allochtonous
B	275	310	Protein-like Tyrosine-like	Autochtonous, resembles tyrosine, free or combined amino acids
C	350	420 – 480	Humic- / Fulvic-like	Humic Terrestrial Allochtonous
T	275	340	Protein-like Tryptophan-like	Autochtonous

Fluorescence intensity relies on molecular structure since fluorescence is a phenomenon whereby molecules are excited at a specific wavelength and thereafter emit photons when they fall back to the ground state. In a study undertaken by Li *et al*. (2017), a decrease in the post chlorination fluorescence intensity of the aromatic protein-like and humic acid-like components was observed, suggesting that humic acid-like materials and protein-like substances are more reactive with chlorine. It was established from FEEM results that humic matter is the precursor of halogen-containing DBPs, and the protein-like substances within the HPO fraction are likely to form nitrogenous DBPs (Li *et al*., 2017).

2.4.6.3 Parallel factor analysis (PARAFAC) modelling

PARAFAC is a statistical multi-way decomposition tool adopted from the field of psychometrics (Harshman & Lundy, 1994). The method can appropriately be used for data of three-way or higher order structures (Murphy *et al*., 2013). **Figure 2-6** represents the three way EEMS dataset of samples where fluorescence constituents can be mathematically separated (Murphy *et al*., 2014). PARAFAC can be utilised to interpret multi-way FEEM data by quantifying and identifying the decomposed constituents. Organic matter fluorescence EEM datasets contain multifaceted combinations of highly-correlated constituents; hence

there is a need to obtain a chemically expressive PARAFAC model (Murphy *et al*., 2013). However software tools are available to apply and supplement PARAFAC analysis (Murphy *et al*. 2013). PARAFAC analyses undertaken by Fasching *et al*. (2014) indicate that the NOM originated from terrigenous organic matter, as evidenced by a preponderence of humic-like components with a high aromatic character.

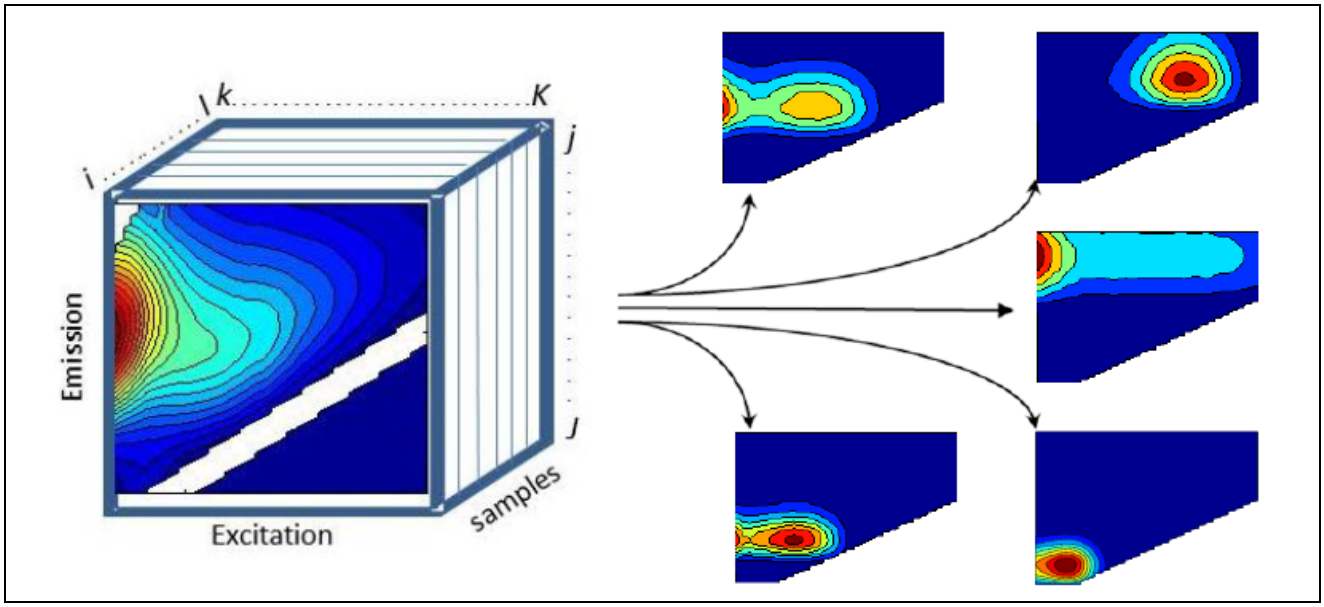

Figure 2-6: Arrangement of EEM dataset in a three-way collection and separated into five PARAFAC constituents (Murphy *et al*., 2013)

PARAFAC modelling has shown effectiveness towards the prediction of the DBP formed by making use of fluorophore constituent scores (Beggs *et al*., 2009; Johnstone *et al*., 2009). In an investigation using PARAFAC showing a correlation between fluorescence intensity, THM formation and chlorine demand seems to suggest strong correlation between quinone-like components and DBPs formed during the chlorination step (Beggs *et al*., 2009).

In a study performed by Pifer & Fairey (2012), PARAFAC modelling was utilised to separate FEEM data into individual fluorophore components and differentiate humic-like from protein-like substances. Pifer & Fairey (2012) also demonstrated the successful application of DOM components to assess the removal of these compounds. By identifying the individual organic matter components, PARAFAC analysis was also applied to investigate the efficacy of the water treatment process and to determine the DBPs formed. A strong positive correlation was observed between the maximum intensity (F_{max}) of one humic-like fluorophore and chloroform formation, as evidenced by an R^2 of 0.84. A moderate correlation existed between F_{max} and $SUVA_{254}$ (R^2 = 0.51). Such a result proves that the PARAFAC fluorescence approach that was adopted in this study serves as an enhancement of the

$SUVA_{254}$ for the identification of DBP precursors since fluorescence analysis appeared to be better predictors of chloroform formation compared to absorbance (Pifer & Fairey, 2012).

In conclusion, the transformation of PARAFAC components in combination with FEEM datasets can therefore be evaluated for each of the different NOM fractions so as to establish the precise precursor responsible for the individual THMs formed (e.g. chloroform, bromoform, BDCM, DCBM).

2.4.6.4 Biodegradable dissolved organic carbon (BDOC)

DOC can be separated into two fractions, namely biodegradable and recalcitrant (non-biodegradable) fractions. Biodegradable dissolved organic carbon (BDOC) is the fraction of DOC that is oxidised by heterotrophic bacteria and quantifies the biodegradable organic matter in water (Crozes & Cushing, 2000; Trulleyová & Rulík, 2004; Axmanová *et al*., 2006). The direct measurement of BDOC entails the measurement of DOC before and after sample incubation using naturally occurring bacteria as the inoculum (Servais *et al*., 1989; Trulleyová & Rulik, 2004).

The principle of the BDOC method is to investigate the decrease in DOC concentration brought about by the oxidation of the carbon by bacteria present in the sample. A typical DOC curve (**Figure 2-7**) is obtained by plotting the DOC values measured over the 6 day incubation period. The refractory DOC (RDOC), also known as non-biodegradable DOC (NBDOC), is obtained when the DOC value reaches a plateau. The BDOC is then calculated when subtracting the RDOC from the initial DOC value (Frias *et al*., 1995; Volk *et al*., 1994). The RDOC value represents the fraction of DOC that was not biodegraded by the bacteria.

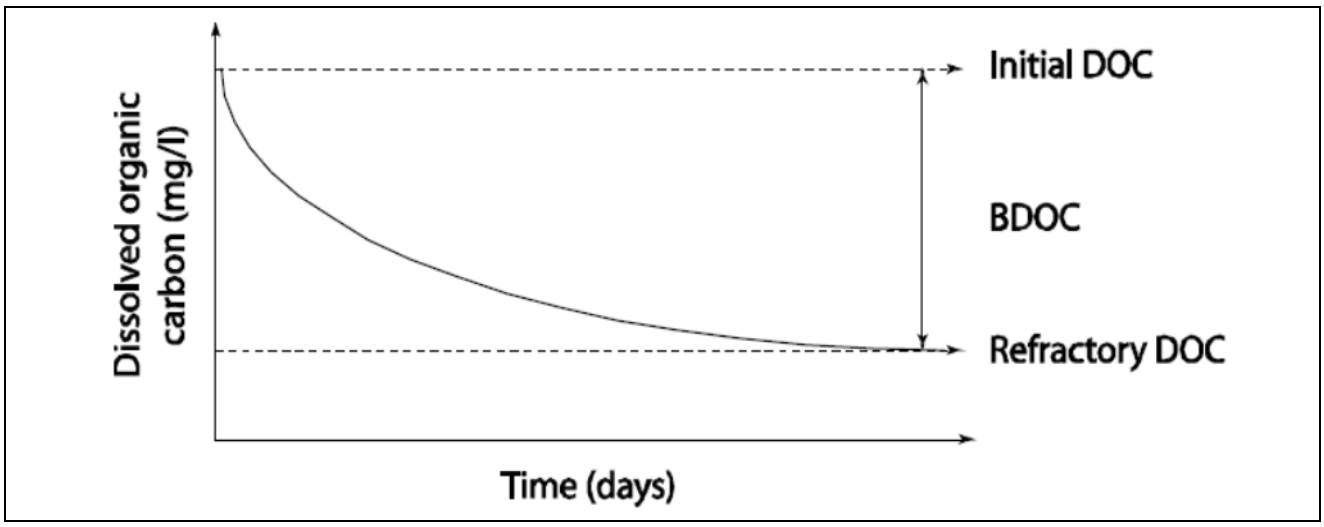

Figure 2-7: Typical curves obtained from a biodegradation study (Ainsworth, 2014)

Servais *et al*. (1989) only evaluated the DOC sample collected just after the inoculum was added and the DOC value at the end of the incubation period (4 weeks). A swift decline in DOC occurred during the first 5 days of the several biodegradation studies. However, a much lengthier incubation period stretching up to before the final DOC reaches a constant value was adopted in other studies (Servais *et al*., 1995; Park *et al*., 2004; Trulleyová & Rulík, 2004; Menge *et al*., 2009). For the method described by Servais *et al*. (1989), an incubation period of 4 weeks before a plateau was reached was chosen. Trulleyová & Rulík (2004) investigated three BDOC methods by comparing results obtained using an inoculum attached to sand, attached to glass beads and suspended in the sample. It was concluded that bacteria attached to the sediment samples (i.e. simulated substrata such as sand) is the preferred inoculum since these bacteria show an increased ability to utilize HMW organic carbon (Park *et al*., 2004; Trulleyová & Rulík, 2004). Furthermore, the use of autochthonous bacteria in BDOC studies is more valuable compared to using a single strain bacterial species; an autochthonous inoculum has a greater capability to degrade DOC (Servais *et al*., 1989).

The absence of BDOC after water treatment limits the possibility of bacterial regrowth in the distribution pipe line. BDOC also provides information that can be correlated to chlorine demand and DBP formation potential (Escobar & Randall, 2002). Hem & Efraimsen (2001) also indicated that a treatment process for the removal of HMW NOM, TOC and colour constituents does not necessarily reduce the biofilm formation potential and that assimilable organic carbon relates more to LMW NOM. It can, therefore, be concluded that the removal of HMW NOM does not always reduce the organic carbon available to bacteria and could therefore still influence bacterial regrowth in the pipe distribution system.

BDOC tests are performed to determine the fraction of organic carbon available within the specific water source that is more readily biodegraded by heterotrophic bacteria. Such tests assist in the selection of improved water treatment options to specifically reduce the labile organic matter, which enhances the re-growth of bacteria in the water supply system (Matilainen *et al*., 2011). The principle to be adopted is to have a treatment option that will effectively remove the biodegradable fraction of NOM. The BDOC assay entails the measurement of decreasing DOC content over a time period due to the mineralisation and degradation of specific molecules within the organic carbon by drinking water bacteria.

Various bacterial decomposition studies have demonstrated the advantage of adding nutrients, nitrates and phosphates to limit nutrient deficiency (Schmidt & Alexander, 1985; Kalbitz *et al*., 2003; Reuschenback *et al*., 2003; McDowell *et al*., 2006). In a degradation study, whereas Amon & Benner (1996) added N and P (as KNO_3 and NaH_2PO_4, respectively) concentrations that were 3 times higher than the ambient concentration, Attermeyer *et al*. (2014) added 1.6 mg/L nitrate and 3.6 µg/L phosphate solution to a water sample containing 7 mg/L carbon (DOC). In the study a specific concentration was added to water by Servais *et al*. (1989) during a method validation study. The measured resultant BDOC values were found to be in agreement with the substrates added, thus successfully validating the method that was used (Servais *et al*., 1989). Also, it is possible that the DOC concentration has an effect on the composition of the bacterial population in the most oligotrophic systems, since bacterial growth is inhibited by substrate concentration (low DOC) (Eiler *et al*., 2003). Furthermore, the C:N ratio is lower in LMW organic matter (and rich in organic nitrogen) compared to the biodegradable HMW substances (Amon & Benner, 1996;) which supports the idea that amino acids within LMW organic carbon are vital bioreactive constituents (Amon & Benner, 1996).

The growth efficiency of heterotrophic bacteria is observed in LMW DOC environments due to limited energy required for mineralization (Battin *et al*., 2008). Not only is the biodegradable DOC concentration important, temperature also plays an important role in “bacterial abundance” because increased bacterial biomass is often observed at increased temperatures (Servais *et al*., 1992). According to Allen *et al*. (2004), the temperature at which aquatic bacterial populations usually grow ranges between 20 and 28 ºC.

In the exponential growth phase of Proteobacteria, the growth was inhibited by low carbon concentrations, as indicated by a hyperbolic response to DOC availability (Eiler *et al*., 2003). Furthermore, biomass was constrained by limited carbon within the substrate, which is indicated by a linear increase between bacteria biomass and DOC. As observed by Eiler *et al*. (2003), changes in DOC concentration have an effect on the composition of bacterial communities 2003 whereby different communities were present upon a reduction in the availability of the carbon. In the same study, α-*Proteobacteria* only colonized in the lowest DOC concentrations, compared to β-*Proteobacteria* which were found in samples that contain a variety of organic carbon concentrations (DOC range: 0.04 to 2.53 mM). Although Axmanová *et al*. (2006) documented that the β-Proteobacteria was dominant in the water samples, the γ-Proteobacteria was more abundant in the smaller molecular weight DOC and the LMW carbon was more accessible to bacteria.

The biodegradable fraction of DOC affects mainly the growth of microorganism (Servais *et al*., 1992). Battin *et al*. (2008) documented that it is the smaller molecular weight components between 0.5 and 1 kDa that are much more profoundly metabolised by bacteria and transported across the cell membrane. Other studies have also established that low molecular carbon is more rapidly utilised thus yielding higher bacterial growth efficiencies compared to larger molecular weight organic matter (Axmanová *et al*., 2006; Khodse & Bhosle, 2011). According to Van Leeuwen *et al*. (2005), it is these HPI LMW carbons that are not easily removed by WTPs. These LMW and HPI NOM fractions are the NOM components that are not easily reduced by conventional treatment processes (Van Leeuwen *et al.,* 2005) and they result in the generation of DBPs after disinfection (Hwang *et al*., 1999; Marhaba & Van, 2000).

Nevertheless, the LMW DOC are not always exclusively degraded; other studies have demonstrated that both fractions are utilised by the bacteria present within the sample (Miller & Moran, 1997; Steinberg, 2013). Steinberg (2013) has indicated that 25% of HMW as well as an additional 10% of the smaller molecular weight DOC were degraded. Amon & Benner (1994) have demonstrated that bacteria degrades the LMW fraction of DOC initially whereafter they degrade the bioreactive HMW organic carbon as well (Amon & Benner, 1994). Growth efficiency appeared to be higher in LMW NOM samples but a larger percentage of the HMW organic carbon was utilised by bacteria present in the sample (Amon & Benner, 1996). This suggests that increased efficiency in bacterial growth during

the BDOC tests does not exclusively indicate a higher degradation of a specific fraction (Amon & Benner, 1996).

Bacteria effortlessly assimilate and metabolize LMW compounds, including carbohydrates, carboxylic acids and amino acids, and are associated with high growth efficiencies (Berggren *et al*., 2010). In a study performed by Volk *et al*. (1997), LMW organic components (carbohydrates and amino acids) were not totally biodegraded as generally expected and respective BDOC values of 40 and 51% were observed. Therefore, it should not be presumed that all carbohydrates are biologically degradable and humic substances are refractory (Volk *et al*., 1997).

According to a size reactivity continuum model shown in **Figure 2-8**, the degradation of NOM in water environments results in the formation of refractory LMW components (Amon & Benner, 1996). The arrows indicate major pathways of degradation from bioreactive constituents towards smaller molecular weight components. The size of the dots represents NOM size, with large dots indicating POM; medium dots indicate HMW NOM and smaller dots represent the LMW organic matter.

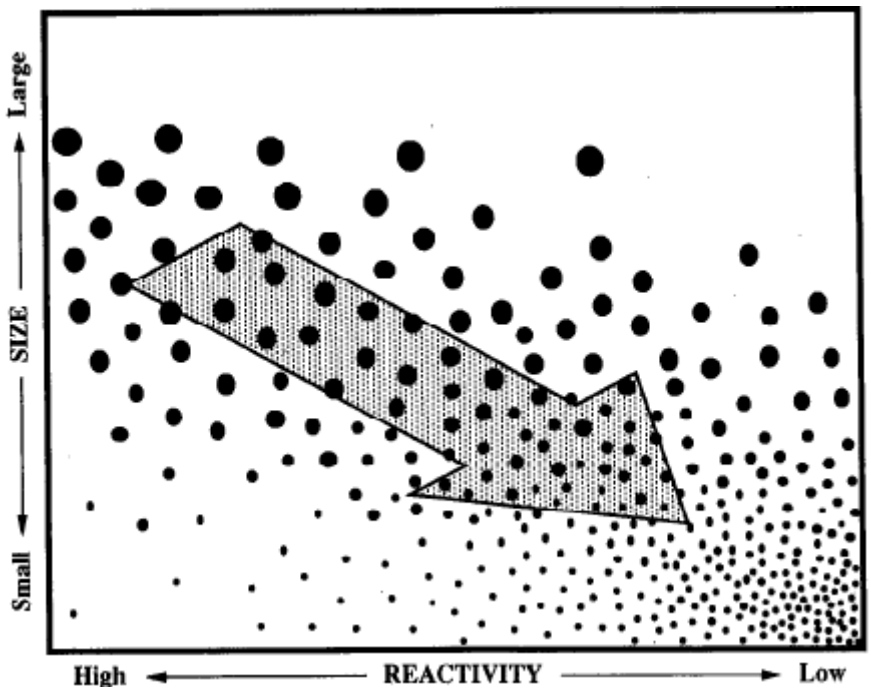

Figure 2-8: Size reactivity model for NOM degradation in water sources (Amon & Benner, 1996)

In conclusion, BDOC tests are performed to determine the fraction of organic carbon available within the specific water source that is more readily biodegraded by heterotrophic

bacteria. Not only is the DBOC method a characterization technique giving alarm to which fraction (HPO, HPI, TPI) are favourably biodegraded, it can also assist the selection of an improved water treatment option to specifically reduce the labile organic matter, which enhances the re-growth of bacteria in the water supply system (Matilainen *et al*., 2011). The objective is to select a treatment option that will ultimately remove the biodegradable fraction of NOM.

Lastly, the BDOC of the specific source water will produce useful insight on the problematic NOM fraction (HPO, HPI, TPI) in terms of bioavailability to heterotrophic bacteria within the WTP and also to provide an enhanced understanding of the correlation or relationship between hydrophobicity and bacterial degradation of these fractions.

2.5 CONTROLLING THE IMPACT OF ORGANIC MATTER IN POTABLE WATER SYSTEMS (TECHNOLOGY FOR NOM REMOVAL)

2.5.1 Treatability of NOM

The key objective and primary intention of NOM removal is to limit the formation of DBPs in the final drinking water supplied to customers. Plourde *et al*. (2015) suggests that treatability of the organic matter should be pre-determined to achieve the best fit THM and HAA control measures as many technologies are site specific (type of source water within a specific location) and depends on the NOM characteristics of the source water.

Due to DBPs having different precursors, the reaction pathway that involves chlorine is specific to each group of the DBP formed during the disinfection step. Researchers therefore recommend that protocols to minimise DBPs should be focused on assessing the precursor in the individual water source and its subsequent DBP formation (Bond *et al*., 2011). There is currently not a singular or all-rounder method that exists that will diminish all DBPs during water treatment. Plourde *et al*. (2015) made use of coagulation (alum and ferric sulphate), IO_3, PAC, magnetic ion exchange and nanofiltration and investigated the impact of these technologies on the characteristics of six surface waters. **Figure 2-9** is a schematic illustration of typical DOC removal percentages achieved when using different removal technologies studies by Plourde *et al*. (2015).

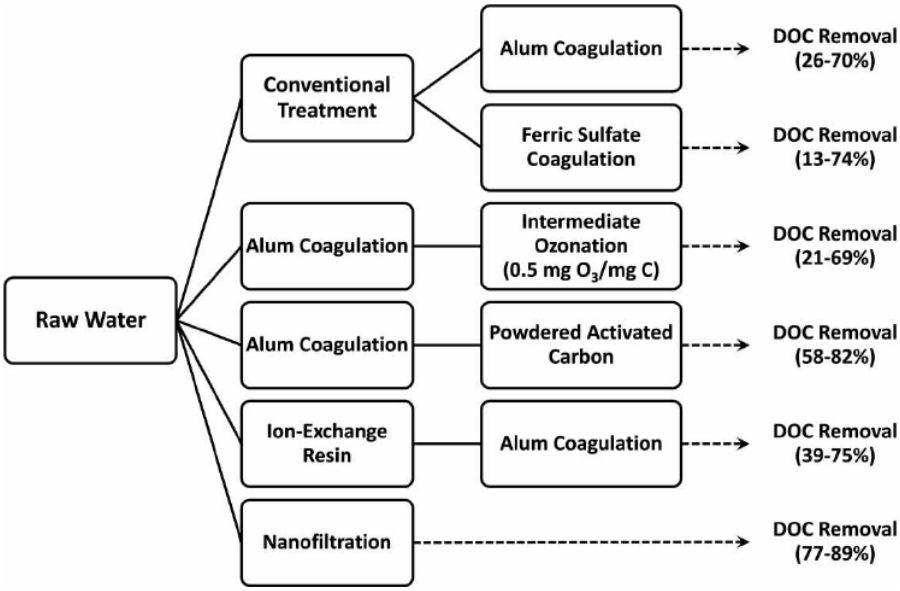

Figure 2-9: Schematic diagram illustrating various treatment options and its typical DOC removal percentages (Plourde *et al*., 2015)

2.5.2 Conventional water treatment

2.5.2.1 Coagulation

It is understood that treatability of DOC can be determined by knowledge of the composition of each of the classes of NOM fractions based on their polarity. The use of coagulants is dependent on source water characteristics as NOM removal depends on the initial concentration of NOM present in surface water (Tubic *et al*., 2013; Plourde *et al*., 2015). To this end, different coagulants remove different DBP precursors. Matilainen (2002) indicated that the use of ferric sulphate is much more effective for the reduction of the LMW NOM fraction (1 to 4 kDa) compared to alum. Ferric sulphate outperformed alum for removal of UV_{254} and DOC in DOC rich waters, but alum is much more effective in water with low DOC (around 3 mg/L).

During potable water treatment, the coagulation step is much more effective in the removal of HMW humic and fulvic components (also referred to as the HPOA fraction) (Krasner & Amy, 1992; Matilainen *et al*., 2002; Sharp, 2006). Chang *et al*. (2004) also observed a 59% reduction in DOC and the removal of the HMW components larger than 30 kDa. When dosing similar amounts of alum and poly aluminium chloride (PACl), the latter seems to be more effective for DOC removal due to PACl having a higher charge neutralisation capacity (Chang *et al*., 2004).

It is well documented that the addition of specific coagulants or flocculants form flocs that settle out together with NOM, depending on the source water characteristics, coagulant dose, coagulant pH and NOM quantity and quality (Parsons *et al*., 2004; Edzwald and Tobiason, 2010). NOM removal by coagulation is attributable to charge density of the HPO fraction (Sharp, 2006; Edzwald & Tobiason, 2010). Increased NOM removal can be achieved depending on the coagulant used. High levels of DOC removal were achieved with a Zr^{4+} coagulant, MIEX plus coagulation and Fenton's reagent compared to when using a Fe^{3+} coagulant (Jarvis *et al*., 2008). Larger flocs were also achieved when using MIEX plus coagulation or Zr^{4+} compared to Fe^{3+} coagulation to an extent that an increase in NOM removal of 37% and 27%, respectively, was noted (Jarvis *et al*., 2008). A coagulant that is superior in terms of NOM removal is the iron based coagulant Ferripol XL, which has the ability to reduce DOC by 80.5% (Jarvis *et al*., 2012). A comprehensive review undertaken by Silaanpää *et al*. (2018) reports that electrocoagulation shows great potential towards the removal of NOM. In a study carried out by Dubrawski & Mohseni (2013), DOC was reduced by 73% and a UV_{254} removal of 88% was achieved. As evidenced by a UV_{254} removal of 94% and a DOC reduction of 81%, the polymeric coagulant polyferric sulphate (PFS) shows a superior performance in the removal of humic acids (Zhao *et al*., 2011).

Other than showing limited removal capacity towards HPI, LMW component of NOM, coagulation is not capable of reducing organic matter fractions of N-nitrosamine precursors (Liao *et al*., 2015). Conventional water treatment often shows excellent removal of HMW organic matter (Amy *et al*., 1992; Nissinen *et al*., 2001; Matilainen *et al*., 2006). In a study conducted on conventionally treated water, Hassouna *et al*. (2014) investigated the contribution of the HPO, HPI and TPI fractions and their potential to form THMs. Results emanating from this study led to the conclusion that the formation of THMs is highly influenced by the HPO fraction. This assumption was supported by a correlation coefficient R^2 of 0.896 that was achieved for THMFP and HPO NOM compounds (Hassouna *et al*., 2014).

Coagulation predominantly removes the HMW NOM, and the removal of the LMW HPI NOM is rarely achieved. Before a specific coagulant is chosen, it is crucial to first investigate the characteristics of the source water and establish the composition of the NOM (Silaanpää *et al*., 2018).

2.5.3 Activated Carbon

2.5.3.1 Powder Activated Carbon (PAC)

Liao *et al*. (2015) made use of PAC, which is generally used in the water industry of China, and concluded that PAC removed more than 90% of the HPO NDMA precursors and 50% of the HPI component of NDMA precursors. However, Szlachta & Adamski (2009) have managed to reduce DOC levels by up to 77.7% and achieve UV_{254} removal by up to 91.0%. Only a small percentage of LMW (< 1.5 kDa) was removed; this was indicated by a 24% increase in NOM removal efficiency, which is possibly due to HMW organics having a high affinity for the activated carbon surface.

When Kristiana *et al*. (2011) combined enhanced coagulation with PAC treatment, a 70% NOM reduction (measured as DOC) was achieved. Although THM formation decreased by 80%, HAAs by 85% and a 95% reduction in the formation of HANs was recorded, an increase in brominated DBP formation was evident. It was concluded that the removal of chlorinated by-product precursors were not directly related to the PAC dosage but were instead more dependent on the PAC type and the source water characteristics.

In a study performed by Plourde *et al*. (2015), PAC treatment were site specific as some source waters had decreased chorine reactivity and smaller TTHM yields. Where other source waters in different regions had increased chlorine reactivity (as high as 71%) that resulted in an increased TTHM formation of up to 48%. Although PAC treatment increased the removal of bulk NOM (as evidenced by DOC and UV_{254} data), only a fraction of the LMW NOM was reduced.

2.5.3.2 Granular Activated Carbon (GAC)

GAC is often preferred over PAC as it preferentially removes the LMW. However, larger molecules can easily block the pores of the GAC adsorption sites thus reducing the removal of organic matter (Pelekani & Snoeyink, 1999; Chang *et al*., 2004). This was confirmed by Matilainen *et al*. (2002) when GAC filtration was applied after aluminium sulphate coagulation. Results of this study revealed that the HMW fraction was not decreased further by the GAC even though the IMW and LMW organics were reduced. Nissinen *et al*. (2001) observed that the use of GAC filtration decreased humic matter somewhat better than when only conventional treatment was used.

Gibert *et al*. (2013) has indicated that DOC removal is not only due to adsorption; the biodegradation from the active bacterial biomass within the GAC filter media also appears to play a role. It is evident from a study undertaken by Baghoth *et al*. (2009) that biological activated carbon (BAC) filtration reduces the DOC fraction of low aromaticity. Overall, GAC treatment provides a good reduction of organics (Thiel *et al*., 2006), which ultimately leads to a huge reduction in the formation of DBPs such as trihalomethanes (THMs) (Chang *et al*., 2004, Wei *et al*., 2008).

2.5.4 Magnetic Ion Exchange Resin (MIEX)

In a study performed by Gan *et al*. (2013) MIEX reduced precursors of THM and HAA by 39-87%, and the IX resin was found to be prone to the removal of the LMW HPI fraction (Bolto *et al*., 2002). A strong base anion exchange resin has proven to lower the DOC concentration and positively influence the coagulant dosage by reducing the amount of alum by 20-60% as well as achieving a DOC removal of 39-75% (Plourde *et al*., 2015). Furthermore, it was found that the PAC outperformed the MIEX/alum treatment method, and this was attributable due to the PAC age and the low resin dosage used; the lowest resin dosage was used as the optimum, achieving an average of 64% DOC removal (Plourde *et al*., 2015). However, the DOC removal occurred when the resin dose was increased (see **Figure 2-9**).

Not only is ion exchange greatly dependent on experimental conditions such as pH and sulphate (SO_4) concentration, it is also site specific. It is therefore essential to incorporate an IX/alum optimization strategy for the specific source water to be used (Plourde *et al*., 2015).

2.5.5 Membrane Technology

Pressure driven membrane technology includes reverse osmosis, ultrafiltration, microfiltration and nanofiltration, which all have individual NOM removal potential (Matilainen *et al*., 2010). Not only does size exclusion and electrostatic repulsion influence NOM rejection, but also NOM aromatic character influences rejection of organic matter by the membrane (Cho *et al*., 1999). Membrane fouling and flux decline are two of the major disadvantages when using membrane technology. Consequently, direct filtration is not desirable and pre-treatment (coagulation) is suggested when considering the use of membrane treatment (Matilainen *et al*., 2010).

2.5.5.1 Ultrafiltration

Kennedy *et al*. (2005) has indicated that the removal of fouling agents originating from the HPI organic matter was problematic, with fouling of the membrane being in the order HPI > HPO > TPI NOM. Nonetheless, polysaccharides (e.g. peptides, amino sugars and proteins) within the HPI fraction having a molecular weight size bigger than 20 000 Da are likely to cause fouling to the membrane as these components are not removed by the PES/PVP hollow fibre membranes (Kennedy *et al*., 2005). Therefore, the NOM fraction of low molecular weight (smaller than 350 Da) not rejected by the membrane do not have the potential to cause fouling (Kennedy *et al*., 2005). Membrane rejection results and NOM fractionation (making use of LC-OCD) generated from the Kennedy *et al*. (2005) study indicates that not all NOM components having a HPI character are of low molecular size.

2.5.5.2 Nanofiltration

Nanofiltration used as direct filtration in low DOC (3 to 8 mg/L) source waters resulted in the highest removals of UV_{254} and DOC (68 to 99%) compared to coagulation, IO_3 and MIEX (**Figure 2-9**). Nanofiltration appears to be the superior treatment technology for the removal of HAA precursor, as evidenced by a HAA concentration below 40 µg/L. In contrast, removal of TTHM precursors were different within the six surface waters tested and appeared to be site specific (Plourde *et al*., 2015).

2.5.5.3 Reverse Osmosis (RO)

The hydrophobicity of DOC is crucial for the treatability of organic matter, as adsorption of the HPO fraction of solutes could take place on the surface of the membrane and thus result in a higher retention of the HPO organics (Hu *et al*., 2003). Rejection of DOC by RO ranged between 49.7% and 95.5%, with the highest removal being the HPO NOM fraction (Hu *et al*., 2003).

2.6 CONCLUSIONS

It is evident from the literature reviewed in this chapter that there is an undeniable need within full scale drinking water production to:

i.) Monitor the bulk organic loading within the particular source water, as NOM character and composition differs not only in source waters but also within

different WTPs of the same country. Seasonal variability relating to temperature and rainfall is also evident which results in inconsistency of the NOM removal efficiency at WTPs.

ii.) Establish NOM removal achieved at the water treatment plant utilising reliable quantitative and qualitative characterization techniques that will generate credible data when investigating alternative treatment technology to enhance NOM removal and ultimately reduce DBP formation.

iii.) Investigate the treatability of the organic matter by incorporating advanced NOM characterization techniques so as to classify NOM according to its main fractions. This will additionally enable the specific precursors responsible for the DBP formation to be identified based on their fluorescence properties, size and hydrophobicity. The change in NOM character after each treatment step is also of great importance since it informs the treatment regime that should be followed for the removal of the various NOM components.

iv.) Establish a sound perspective regarding the conflicting correlations that exist in the literature between, for example, TTHM formation potential and aromaticity (UV_{254}) and between DOC and aromaticity. It is also important to investigate the NOM component that is specifically responsible for THMs and establish the most biodegradable fraction that influences biological regrowth in distribution systems.

v.) Propose a NOM protocol that indicates which parameters and characterization techniques and the frequency thereof should be incorporated into the monitoring programme of a full scale plant. It is of utmost importance to assess NOM character in the specific source water and to continuously evaluate NOM removal achieved by the WTP. This will allow for control measures to be employed when episodes of increased NOM in the source water is experienced. This could possibly be incorporated into water safety planning (WSP).

In the chapters that follow, thorough attention will be given to specific aspects that are highlighted above.

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CHAPTER 3: EXPERIMENTAL METHODOLOGY

3.1 INTRODUCTION

This chapter outlines the experimental design and methods followed in achieving the objectives of this study. All experimental procedures followed as well as method development (**Sections 3.4.2** and **3.6.3**) are described in this chapter.

3.2 SAMPLING SITE

3.2.1 Description of sampling area

The Vaal Dam is a 324 km^2 impoundment situated in the Free State province of South Africa and is used as the source water for two of Rand Water's treatment plants situated in Gauteng. Being the bulk water service utility in South Africa, Rand Water (RW) (supplies 4.2 million m^3/d drinking water to an average of 13 million people, including various municipalities, industries and mines. The two RW treatment plants are Zuikerbosch Water Treatment Plant (ZWTP) and the Vereeniging Water Treatment Plant (VWTP). While the ZWTP receives its source water mainly in a canal open to the elements, the VWTP receives its water in a closed pipeline. Rand Water (previously known as the Rand Water Board) was established in 1903, and the two WTPs jointly supplies water through a 3500 km pipe distribution network, to mainly the Gauteng and Free State provinces as well as a town in the Mpumalanga Province, which is situated 150 km from ZWTP.

The RW treatment plants utilise conventional water treatment where DOC removal is achieved by coagulation/flocculation, followed by sedimentation and rapid gravity sand filtration. **Figure 3-1** provides an overview of the conventional treatment process and the location of the various sampling points as indicated by the yellow circles. Sampling point 1 represents source water from the Vaal Dam sampled at the intake of the WTPs. The Vaal Dam source water quality is characterized by medium colour, medium turbidity, pH range of 6.5 to 8.5 and a moderate DOC concentration (3.0 to 7.0 mg/L).

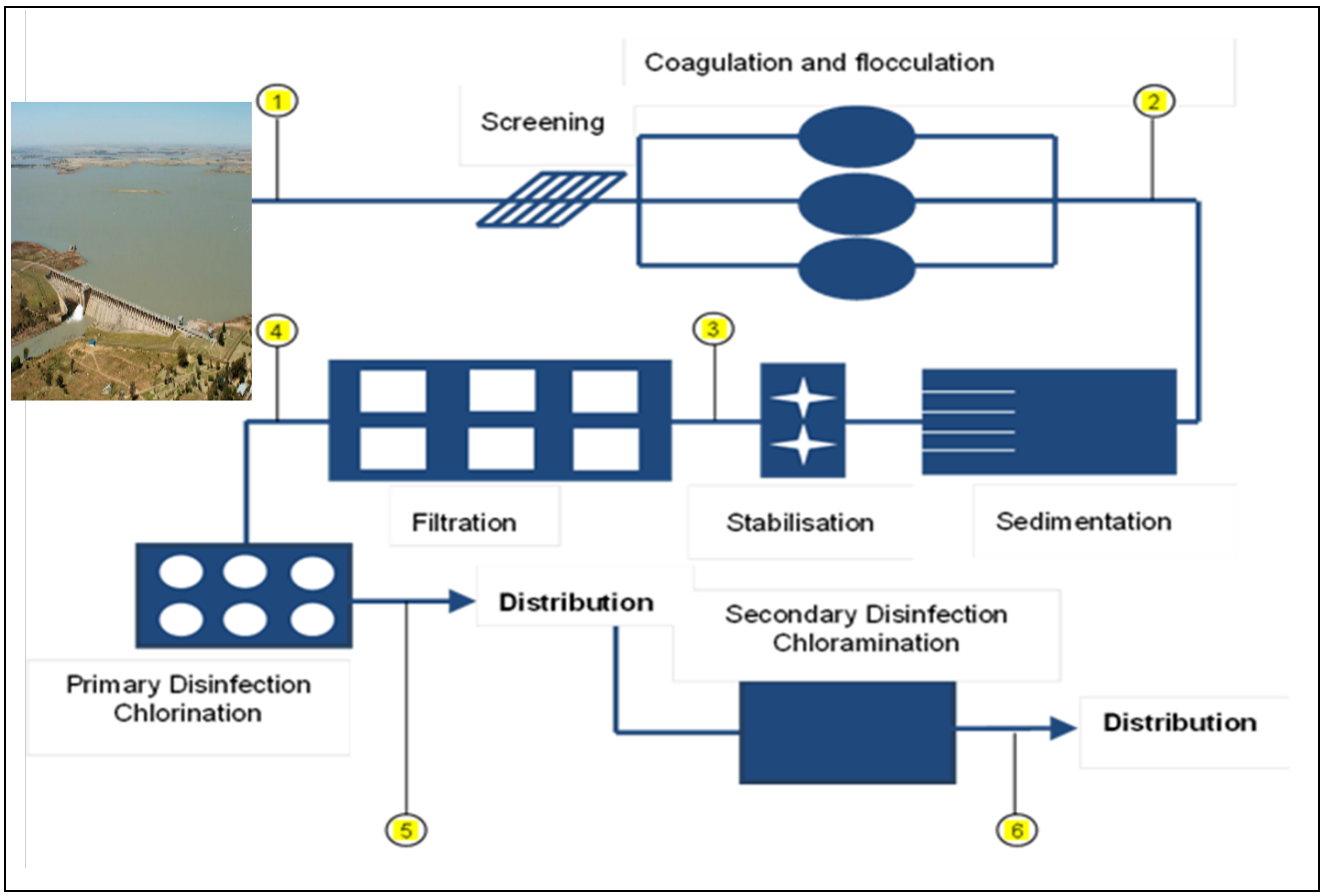

Figure 3-1: Illustration of the conventional treatment process and locality of the sampling points

3.2.2 Sample collection, frequency and storage

Source water samples were collected at the intake of the two full scale RW treatment plants on a fortnightly basis to evaluate bulk NOM characteristics, incorporating all four seasons over a five year monitoring period. Following the full scale rapid sand filtration and disinfection (chlorination and chloramination) steps, the water was sampled during summer (December to February), autumn (March to May), winter (June to August) and spring (September to November) so as to include NOM seasonality and variability in organic loading or change in reactivity due to summer rainfall or surface run-off. Samples were transported in a cooler box to the laboratory whereafter the samples were refrigerated at 4 ºC for a maximum storage of 1 day.

All chemicals utilised during this study were of analytical grade and all standard solutions were prepared using deionized water (Milli-Q system, Millipore).

3.3 BULK (QUALITATIVE) NOM CHARACTERIZATION

Advanced NOM characterization techniques were performed on a seasonal basis during the duration of this study to incorporate possible NOM seasonality and were also used in the NOM characterization and monitoring protocol (**Figure 3-5**).

Conductivity and pH were analysed using a Mettler Toledo (DHL-53) with colour and turbidity determined by a photometer (HACH 2100AN). All these parameters were measured in the laboratory after the samples were kept at 4 ºC.

3.3.1 Dissolved organic carbon (DOC)

Samples were filtered through a membrane filter (0.45 µm) whereafter DOC was measured with a Shimadzu TOC-L analyser to determine the bulk organic carbon loading in Vaal Dam surface water samples. Standard carbon solutions were utilised to calibrate the instrument making use of hydrogen phthalate (KHP) of concentrations of 1 mg/L, 5 mg/L, 10 mg/L, 20 mg/L and 30 mg/L. Three replicates of a measurement were performed averaging the results obtained. The removal effectiveness of NOM by the treatment plant was also quantified as the percentage DOC reduction after the various treatment steps (coagulation, sedimentation, sand filtration).

3.3.2 Ultraviolet absorbance at 254 nm (UV_{254})

After filtering the samples through a 0.45 µm filter (Millipore), UV_{254} was measured using a spectrophotometer (Agilent Technologies Cary 60 UV-Vis) to determine the aromaticity of the NOM in the surface water sample. The absorbance of water sampled after full scale coagulation and sedimentation was measured at wavelength 254 nm (UV_{254}) to determine overall removal of NOM and efficiency of these conventional treatment steps. The character of the three fractions (hydrophobic, hydrophilic, transphilic) obtained through the polarity rapid assessment method (PRAM) was also analysed using UV_{254} measurement. Due to the organic matter structure consisting of double bonds between the carbon atoms that absorbs ultraviolet light at this wavelength (254 nm), the UV_{254} measurement was used as an indication of the aromatic quantity of NOM (Edzwald & Tobiason, 2010).

3.3.3 Specific ultraviolet absorbance (SUVA)

The SUVA values were calculated according to **Equation 3.1** after obtaining the DOC and UV_{254} measurements. The SUVA value indicates the composition of NOM in the sample with regards to its aromatic character (Edzwald & Tobiason, 2010). SUVA indicates the amount of humic substances present in organic matter relative to non-humic substances SUVA also indicates the amount of humic substances in relation to non-humic substances present within the organic matter (Weishaar *et al*., 2003). Owing to a strong correlation that exists between SUVA and humic matter removal and TTHM formation, the SUVA value of a source water sample provides the benefit of predicting the treatability of the water. SUVA is also a valuable NOM surrogate parameter.

$$SUVA\ \left(L/mg.m\right)=\frac{UV_{254}\left(cm^{-1}\right)\times 100\frac{cm}{m}}{DOC\left(\frac{mg}{\ell}\right)} \qquad [3.1]$$

3.3.4 High performance size exclusion chromatography (HPSEC)

The change in the arrangement of the molecular sizes of humic organic matter, which is known as molecular size distribution (MSD), is a rapid and dependable method to demonstrate the efficiency of a treatment process in terms of NOM removal (Myllykangas *et al.,* 2002; Li *et al*., 2013). The distribution of the molecular size fractions was investigated using the high performance size exclusion chromatography (HPSEC) method described by Nissinen *et al*. (2001).

Samples were filtered through a 0.45 µm syringe filter and 20 µL was injected into a Hewlett Packard 1100 HPLC system. The molecular weight fractions were divided using a TSK G3000SW column (7.5 mm x 300 mm) using 0.01 M sodium acetate as mobile phase and at a flow rate of 0.7 mL/min. A guard column of 70 mm of the same phase was used to safeguard the column. After detection at 254 nm the peak area of each fraction was determined. The various peaks are expressed on the chromatograms in milli absorbance units (mAU), indicating the peak height against time (minutes) that the various molecular sized molecules were eluted.

Generally six NOM fractions (peaks) are eluted, with peaks I - II representing the HMW fraction and peaks III - IV representing the intermediate molecular weight fraction. Peaks V and VI illustrates the presence and quantity of LMW organic matter (Vuorio *et al*., 1998,

Nissinen *et al*., 2001). The HMW fraction indicates the humic and fulvic compounds of terrestrial origin and the smaller molecular sized NOM indicates non-humic organic matter (Szabó & Tuhkanen, 2007).

3.4 NOM FRACTIONATION BY SOLID PHASE EXTRACTION

The variation in polarity of organic matter in water samples can be evaluated by using non-polar, polar and anion exchange solid phase extraction (SPE) cartridges. This is achieved by measuring the UV_{254} of the samples, which enables the evaluation of the amount of organic material adsorbed onto the individual cartridges (Rosario-Ortiz *et al*. 2004). The NOM characterization technique that divides the organic matter into three major fractions instead of the original six fractions is known as the modified polarity rapid assessment method (m-PRAM). This technique was modified by Nkambule *et al*. (2012) and is a less time consuming method than the original PRAM by Rosario-Ortiz. This method fractionates NOM into a HPO, hydrophilic HPI and transphilic (TPI) fraction as these three fractions best represent the composition of the NOM with respect to its aromaticity (Nkambule *et al*., 2012).

The modified-polarity rapid assessment method (m-PRAM) were utilised in this study to divide NOM into the HPI, HPO and TPI fractions (Nkambule, 2012). The apparatus that was used for m-PRAM is a 24 position vacuum manifold (Phenomenex) connected to a vacuum pump and 20 mL glass vials for collecting the SPE filtrate (**Figure 3-2**). The three cartridges for m-PRAM are C18 (non-polar cartridge to obtain HPO fraction), CN (polar cartridge to obtain HPI fraction) and NH_2 (weak anion exchange cartridge to obtain TPI fraction). The size of the SPE cartridges that was used is a 500 mg sorbent in a cartridge volume of 6 mL.

This fractionation method was combined in a similar cleaning procedure described in Chen *et al*. (2014) that added methanol to the cleaning procedure of the cartridges. The methanol cleaning step will enhance recovery of the NOM fractions by the cartridges but more critically, is an attempt to limit organic carbon leaching from the cartridges into the filtrate during the elution step. The leaching of carbon from the SPE cartridges during the early stages of PRAM optimisation was documented in previous studies (Nkambule, 2012; Chen *et al*., 2014).

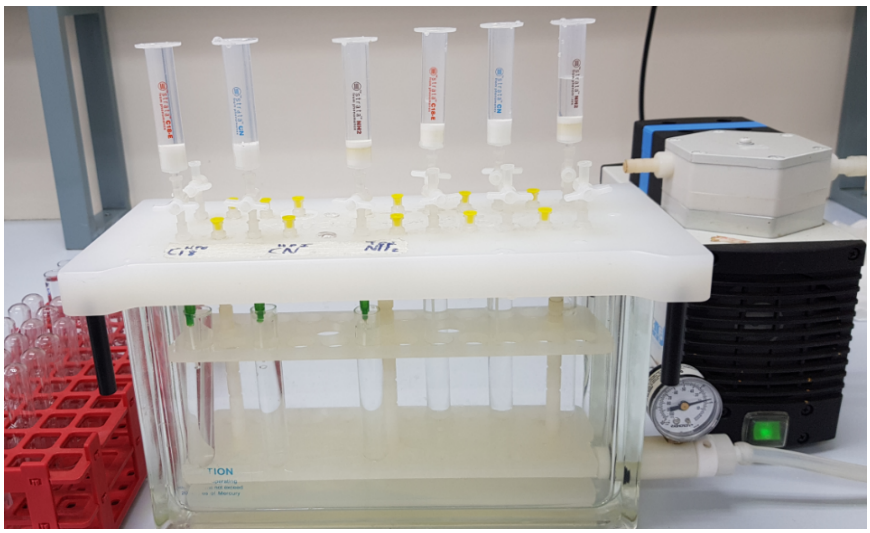

Figure 3-2: Vacuum manifold with SPE cartridges used for m-PRAM

3.4.1 Experimental procedure for modified polarity rapid assessment method (m-PRAM)

Milli-Q water was filtered through the three SPE cartridges to clean the cartridges from any UV absorbing material that might be present in the cartridges until a steady-state UV_{254} was obtained, as indicated by a UV_{254} value that is close to zero. A steady-state UV_{254} reading occurred after flushing with Milli-Q water at a flow of 1.2 mL/min for a 15 minute period following a procedure described by Rosario-Ortiz *et al*. (2007).

The second step in the m-PRAM analysis involved obtaining the breakthrough curve from each SPE cartridge on the sample analysed. The sample was first filtered through a 0.45 µm membrane filter (Whatman) and thereafter filtered through the three cartridges at a flow of 1.2 mL/min (5 inches Hg, 0.1 bar). The experimental set-up is illustrated in **Figure 3-3**. A volume of about 10 mL 0.1 M NaOH was filtered through the C18 and CN cartridges to elute the HPO and HPI fractions, respectively. The filtrate of the C18 cartridge (prior to eluting the HPO fraction) was filtered through the CN cartridge and was finally filtered through the NH_2 cartridge to obtain the TPI fraction, which indicates the anionic character of the organic matter.

The m-PRAM experiments were performed in duplicate on the source water, water after full scale sand filtration and on the final treated water, with the results presented as retention coefficient (RC) of each SPE sorbent. The RC portrays the fraction of UV_{254} absorbing material within the samples that was adsorbed onto the various cartridges after initial

breakthrough occurs. The RC value is calculated as one minus breakthrough divided by the initial UV_{254} absorbance of the sample before PRAM fractionation (**Equation 3.2**).

$$RC = 1 - \frac{C_{max}}{C_0} \quad [3.2]$$

where RC is the retention coefficient, C_{max} is the maximum breakthrough obtained during the extraction and C_0 refers to the UV_{254} value of the original sample before fractionation (Rosario-Ortiz *et al*. (2007).

3.4.2 Optimisation of modified-PRAM (m-PRAM)

In this study, another component was added to the washing steps of the m-PRAM. The additional component entails the 2 column volumes of methanol that was added to the C18 and CN cartridges in an attempt to elute the uncombed organic carbon from the cartridges that are otherwise not eluted by washing with Milli-Q water alone (Chen *et al*., 2014). Milli-Q water was then filtered through all three SPE cartridges until a steady-state UV_{254} was obtained. This occurred after flushing at least eight column volumes of Milli-Q water through the various cartridges for a 15 minute period. UV_{254} measurements were carried out on methanol before and after filtering through the C18 and CN cartridges. Absorbance curves were obtained for each SPE sorbent (C18, CN and NH_2) after passing methanol and Milli-Q water through the cartridges and measuring the UV_{254} at various time intervals within the 15 minute cleaning procedure. UV_{254} measurements were also obtained during the washing step of C18, CN and NH_2 while passing only Milli-Q water through without prior methanol addition.

The supernatant from each SPE cartridge was then analysed by UV_{254} and DOC. The UV_{254} data was used for the treatability study which indicates the NOM fractions removed by the treatment steps as well as the percentage of aromatic NOM present within the various samples. The DOC values were used for a mass balance calculation in order to determine leaching from the cartridges and recoveries of organic carbon by the various cartridges.

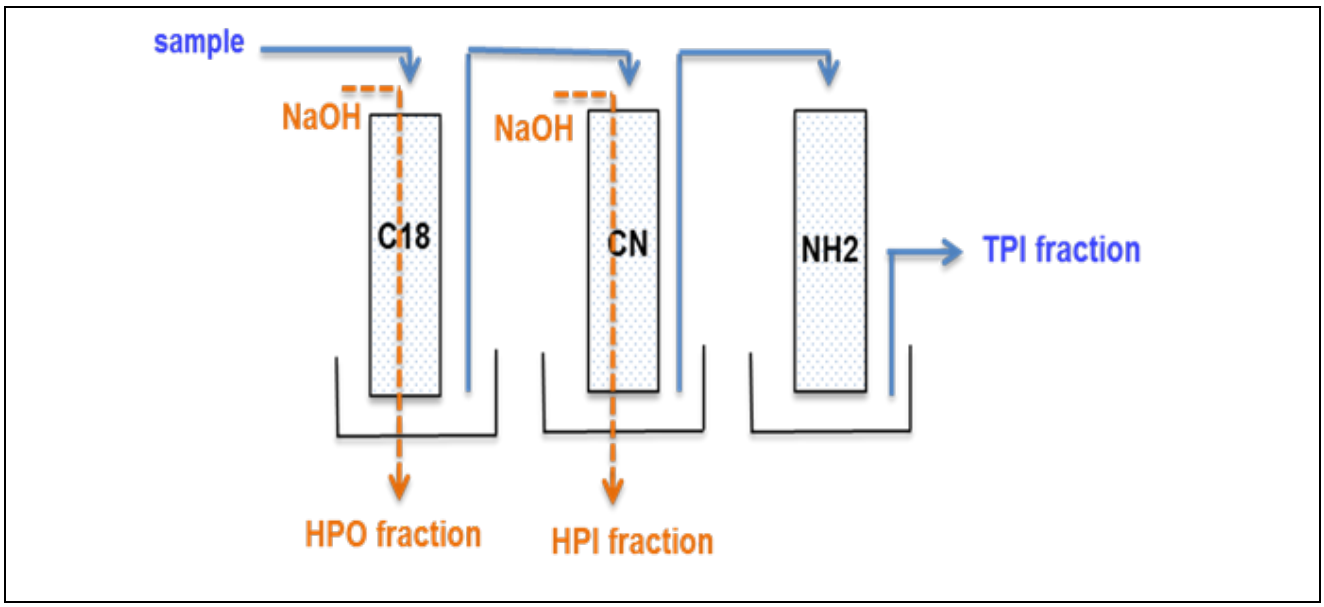

Figure 3-3: Experimental set-up for m-PRAM

3.5 ADVANCED NOM CHARACTERIZATION USING FEEM

The analytical instrument performance of fluorescence emission and excitation spectroscopy is greatly sensitive and selective and simultaneously measures emission and absorbance of fluorescence compounds (Gilmore, 2014). FEEM has the advantage of determining the origin of humic compounds (both humic-like and protein-like) and will assist to evaluate the treatability of NOM by evaluating whether the NOM component is removed by the treatment step.

A Horiba AquaLog spectrometer was used by exhibiting an emission intensity of 1000 arbitrary units (AU) and making use of a xenon exciting light source where emission excitation slits were at a band pass of 10 nm. By increasing the excitation wavelengths with 5 nm steps from 200 to 800 nm, the excitation emission matrix was obtained, where emission at extended wavelengths are usually detected with 0.3 nm increments. In an attempt to account for Raleigh scattering lines, subtraction of the fluorescence background of the solution is required (Gilmore, 2014). This was achieved by subtracting the blank solution from the fluorescence spectra of the water sample to be analysed. A solution of a predetermined DOC dissolved in deionised water was used as the blank to also account for inner filter effects due to organic carbon molecules that absorb light from the lamp. The transmission detector was then used to record the absorbance transmission spectrum of the various samples under equal resolution and spectral-band pass as the excitation emission data. The corrected excitation emission matrices were plotted by the spectrometer

making use of 20 contour lines, with each contour representing a twentieth (1/20) of the maximum fluorescence intensity.

3.6 BACTERIAL DEGRADATION OF NOM FRACTIONS

3.6.1 Experimental procedure for 6 day BDOC analysis

The constraint associated with using a single strain of bacteria is that a single species prefers mineralisation and degradation of specific molecular weight NOM fractions or carbon sources (Amon & Benner, 1996; Mishra & Srivastava, 1998; Axmanová *et al*., 2006). Therefore, filter sand from Rand Water's full scale filters containing a mixed consortium of bacteria was utilised during the BDOC measurements. The filter sand also represents bacteria already present in the WTP under investigation.

An inoculum of sand containing biologically active sand (BAS) was collected from a rapid gravity sand filter from a Rand Water filter house. The sand was transferred to a fish tank in the laboratory and covered with source water until the BDOC tests were performed, as indicated in **Figure 3-4**. The sand in the fish tank was incubated for 7 days by adding fresh source water. A top layer of sand was collected from the filter bed just before the sand filter required backwash, since the top layer of the filter bed is where biological activity is most abundant. The sand was washed using a rinsing solution of 0.1 M sodium thiosulphate and thereafter inverting the sand until no DOC was released from the sand (**Figure 3-4**). The rinsing solution consisted of 10 ml sodium thiosulphate and 490 mL deionised water and the sand was washed at least 10 times to remove organic carbon.
A sample of the washed sand in deionised water was analysed for DOC and used as background DOC.

Six washed sand samples of 100 g were placed in 500 mL Schott bottles whereafter 300 mL of sample were added. Three of the samples consisted of HPI, HPO and TPI fractions obtained from the PRAM technique on the Vaal Dam source water. Three solution concentrations of sodium acetate (5 mg/L, 8 mg/L and 10 mg/L) were used as control; this served to indicate whether the bacterial consortium cultivating the sand was biologically active. Various studies have suggested the use of sodium acetate as a source of carbon in biodegradation studies due to the high biodegradability of sodium acetate by heterotrophic bacteria (Escobar & Randall, 2001; Park *et al*., 2004; Yapsakli & Çeçen, 2009).

Addition of acetate and glucose during BDOC investigations are known to intensify and improve bacterial activity (Yapsakli & Çeçen, 2009).

Figure 3-4: BDOC set-up

Sample bottles were closed with a Schott screw cap and connected to a compressor where air was passed through each sample at approximately 50 mL/min (1 to 2 bubbles per second), as described by Reuschenbach *et al*. (2003). A second tube was fitted to each screw cap to vent air to the atmosphere whereafter the bottles were incubated at 20 ˚C in a water bath for a period of 6 days, measuring the initial and final DOC levels. The BDOC set-up is shown in **Figure 3-4**.

3.6.2 Method development for enhanced BDOC analysis

The procedure outlined in **Section 3.6.1** was followed with the exception that nitrogen (N) and phosphorous (P) nutrients were added to the samples. Nutrient limitation is possible during biodegradation studies and this is shown by an increase in the DOC of the sample brought about by the lysis of microbial cells (Volk *et al*., 1994; Menge *et al*., 2009).

Various studies have performed a biodegradation test by supplementing the sample with inorganic nutrients in order to ensure that the solution is not nutrient limited (Kalbitz *et al*., 2003; Reuschenbach *et al*., 2003; McDowell *et al*., 2006). The addition of nutrients has also been documented by Attermeyer *et al*. (2014) when investigating increased bacterial decomposition by increasing the organic carbon (of allochthonous and autochthonous origin). In this study, it was concluded that the chemical quality of water is more important for DOC turnover by bacteria than the origin of the organic carbon. For the enhanced BDOC investigation, an inorganic nutrient solution with additions of N and P (0.1% KH_2PO_4 and 0.1% NH_4Cl) was prepared to ensure carbon as the only limiting factor in the DOC degradation study. The ratio of sample to BAS that was used in the enhanced BDOC tests was 3:1, whereby 300 mL sample and 50 mL of the inorganic salt solution was added to 100 g sand in 500 mL Schott bottles.

Allen *et al*. (2004) have observed that water based bacteria grow optimally at a temperature of between 20 and 28 ˚C and incubation time of 5 to 7 days. During the enhanced BDOC test, the incubation temperature was increased from 20 ˚C (as per original method of Joret *et al*., 1989, Page & Dillon, 2007) to 30 ˚C. Temperature is known to control the metabolism rate and growth of microorganisms since increased bacterial activity is observed at higher temperatures (Sridevi & Lakshmi, 2009; LeChevallier *et al*., 1996; Bitton, 2014). Gram-negative aerobic *Pseudomonas* optimally grow at temperatures between 25 ˚C and 30 ˚C (Sharp, 2004).

3.7 TRIHALOMETHANE FORMATION POTENTIAL (THMFP)

THMFP is known as the maximum THM formed in a sample under controlled laboratory conditions (pH, temperature, contact time) and ensuring a free-chlorine residual at the end of the laboratory incubation period. The purpose of using this method was not only to determine the main fraction responsible for the THMs formed, but to also determine how the THMFP of these fractions relate to surrogate parameters (UV_{254}, SUVA and DOC). This was mainly achieved by fractionating the NOM into the three major NOM fractions using m-PRAM (**Section 3.5**) whereafter the DBP formation potential studies were carried out by chlorinating the individual NOM fractions (**Section 3.7.6**) and quantifying the DBPs formed (**Section 3.7.7**).

Solid phase extraction and a Headspace Sampler (Agilent 7697A) coupled to a gas chromatograph (Agilent 6890N) were used to analyse the trihalomethanes. The four THMs determined in the final water samples were: bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform and chloroform. Their sum (TTHM in µg/L) as well as the individual concentrations was stated. The detection limits were as follows: BDCM 0.27 µg/L, DBCM 0.33 µg/L, bromoform 0.36 µg/L and 0.21 µg/L for chloroform. A Capillary gas chromatography column (J & W Scientific, 30 mm x 0.530 mm x 0.5 µm) was used to separate the THMs, which were detected using an electron capture detector (ECD). The THMs analyses involved the quantification of bromoform, chloroform, DBCM and BDCM. The THM formation potential was calculated by subtracting the initial THM measured after 30 minutes ($THM_{initial}$) from the final THM after the 7 day incubation period (THM_{final}).

3.7.1 Experimental setup for trihalomethane formation potential (THMFP)

Results of THMFP experiments were conducted on raw water from the Vaal Dam during all four seasons and were compared with THMFP results of the treated water. Water sampled after the sand filtration step represents the treated water samples and was sampled at Rand Waters's full scale treatment plant. Samples were first fractionated into the HPO, HPI and TPI organic matter fractions using PRAM. After chlorinating the individual NOM fractions to achieve a residual free-chlorine concentration of between 3 and 5 mg/L, the samples were submitted for THM analysis after the 6 day incubation period. Extraction of the 4 main THM species ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$) was achieved using a fully automated Headspace Gas Chromatography-Electron Capture Detector (GC-ECD) method. Internal (or more accurately, the surrogate standard) were used to assist with quantitation. The detailed method is discussed within this Section.

3.7.2 Fractionation method

Chemical fractionation into HPO, HPI and TPI organic matter fractions was performed on source water and treated water samples obtained during the summer, autumn, winter, and spring months using the PRAM technique described in **Section 3.4**.

3.7.3 Labware preparation

A chlorine solution of 11% (110 000 mg/L) NaOCl was diluted 100 times to obtain a working stock solution of 1100 mg/L (stock solution A). This was achieved by adding 10 mL of the 11% solution to 1 L deionised water. The actual amount of chlorine of stock solution A was measured at 925 mg/L. This was obtained by further diluting the stock solution to allow the Hach Pocket Colorimeter measurements, which are limited to free chlorine measurements of below 2 mg/L. The N,N-Diethyl-1,4-phenylenediammonium (DPD) free reagent powder was added to a 10 mL sample in the chlorine test vial, shaken for 20 seconds and the free chlorine measurement was thereafter read from the Hach meter. The reading was multiplied by the dilution factor and the actual free chlorine of stock solution A was calculated as 925 mg/L.

Chlorine demand-free glassware was prepared by soaking all glassware in a 4 mg/L chlorine solution. The chlorination experiments were performed in amber glass vials (45 mL) with Teflon-lined septa (PTFE) screw caps, which were also soaked in this bucket prior to incubation. The glass cleaning solution was prepared by adding 7 mL of the 11% NaOCl solution in a 20 L bucket. All glassware was soaked overnight and during the chlorine measurements within the 20 L bucket. Before using the chlorine demand free graduated pipettes, glass beakers and volumetric flasks, the glassware was thoroughly rinsed with deionized water.

3.7.4 Test plan to determine the THMs formed

A test plan was identified to investigate the potential of each NOM fraction to form THMs. All variables were kept constant for all samples in order to compare the THMs formed under the same test conditions. A fixed pH, sample temperature, chlorine dose and contact time was maintained throughout the experiments. A standard reaction condition of 7 days incubation period, pH at 8.3 ± 0.2, and a temperature of 25 ± 0.2 °C and a remaining free chlorine residual between 3.0 and 5.0 mg/L was used. This incubation test and chlorine dosage was not done to simulate the treatment plant/ full scale environment. Therefore, chlorine was overdosed in order to calculate the likelihood of each of the three NOM fractions to potentially form THMs.

3.7.5 Chlorine dosing calculation

The following formula (see **Equation 3.3**) was used to calculate the volume of chlorine stock solution. A stock solution with a concentration of 925 mg/L was added to the various bottles to obtain a chlorine concentration of 12 mg/L in the 45 mL amber bottles.

$$C_1V_1 = C_2V_2$$

$$925\left(\frac{mg}{\ell}\right) \times V_1 = 12\left(\frac{mg}{\ell}\right) \times 45m\ell$$

$$V_1 = \frac{12\left(\frac{mg}{\ell}\right) \times 45m\ell}{925\left(\frac{mg}{\ell}\right)} \qquad [3.3]$$

$$= 0.6m\ell$$

Each 0.6 mL of chlorine dosing solution (stock solution A) as prepared in **Section 3.7.3**, will add 12 mg/L Cl_2 to the 45 mL sample.

3.7.6 Chlorination procedure

The values of DOC, UV_{254}, UV_{274} and pH were determined for each sample before the incubation period. The pH of the samples was buffered to a pH of 8.3 using a borate buffer (1 N H_3BO_3). Chlorine demand free bottles that were prepared in **Section 3.7.3** were rinsed with the water sample under investigation. Each 45 mL glass amber vial was filled with approximately 40 mL of the sample. The chlorine dosing solution was added to the samples using a 2 mL graduated pipette. The bottles were covered with the screw caps containing Teflon-lined septa (PTFE) and inverted for a thorough mix. After mixing, the bottle was filled with the sample until it overflowed. This was done to ensure that there is no headspace between the sample and the cap at the start of the incubation.

After 30 minutes the residual chlorine was measured. During each free chlorine measurement, 1 mL of the sample was withdrawn and filled with deionized water to a volume of 10 mL. The sample was transferred to the chlorine test vial and DPD powder was thereafter added and shaken for 20 seconds. The reading displayed on the Hack Pocket Colorimeter was multiplied by a dilution factor of 20 to obtain the residual free chlorine concentration within the samples. After the 7 day incubation period, ascorbic acid was added to the samples to quench the residual chlorine and stop further formation of disinfection by-

products, whereafter the THMs were measured on all samples as described in **Section 3.7.7**.

3.7.7 THM analysis by Gas Chromatography Electron Capture Detection (GC-ECD)

3.7.7.1 Introduction

The principle of this method is that samples are heated in a sealed vial to drive the equilibrium of the THMs into the gas phase. An aliquot of this THM-rich gas phase is transferred via a heated transfer line to the gas chromatograph (GC) where the THMs are separated into individual components as they pass through the GC column. An electron capture detector (ECD) is used to detect the individual THMs and aid in their quantitation.

3.7.7.2 Preparation of Standards

- *Internal standard (ISTD)*

The internal standard (ISTD) (46 µL of 1,2-Dibromoethane) was transferred to 80 mL of methanol contained in a 100 mL calibrated A-grade volumetric flask. The volumetric flask was then filled to the mark with methanol, stoppered and mixed thoroughly by inversion. This solution, which contains (1 µg/mL) of the internal standard, is regarded as the stock standard ISTD and is stable for 1 year. The working standard was then prepared by diluting the stock standard 200 times (200 µL up to 100 mL with methanol) to give a final concentration of 0.005 µg/mL (stable for 3 months).

- *Stock standard*

From a purchased, pre-mixed THM standard (0.2 mg/mL), 500 µL was transferred into a 20 mL volumetric flask and filled to the mark with methanol to make 5 µg/mL.

- *Working calibration and verification standard solutions (chlorine and volatile free water)*

Milli-Q water (2 L) in a glass beaker was placed on a stirrer/hotplate. A nitrogen gas tube was inserted in the beaker and nitrogen was bubbled through the boiling water, allowing the water to boil and evaporate to about half its original volume. The water was cooled before use. After adding 80 µL of ISTD into headspace vials containing 10 mL chlorine free water, a stock standard solution (concentrations ranging 10, 20, 40, 80 and 160 µL of the 5 µg/mL) was added to prepare calibration standards with the following concentrations 5, 10, 20, 40

and 80 µg/L. The ISTD (80 µL) and the 5 µg/mL verification stock solution (30 µL) was added into the headspace vials containing 10 mL chlorine free water sample.

3.7.7.3 Preparation of samples

Using a calibrated A-grade pipette, 10 mL of the sample was accurately transferred to a 20 mL headspace vial, whereafter a volume of 80 µL of working ISTD was injected. A crimper tool was used to ensure that the cap was tightly sealed.

3.7.7.4 Instrument setup

The GC parameters (Agilent 6890N GC-ECD) are listed in **Table 3-1**.

Table 3-1: GC operating conditions

Oven	
Temperature	40°C isothermal
Run time	10 min
Front inlet	
Mode	Split
Initial temperature	250°C
Pressure	3.30 psi
Spilt ratio	10:1
Split flow	51.1 mL/min
Capillary column	
Column type	HP 1 (or equivalent)
Column dimensions	30 m x 0.530 mm x 0.5 µm
Mode	Constant flow
Flow	4.9 mL/min
Front detector	
Type	ECD
Temperature	315°C
Mode	Constant make-up flow
Make-up flow	30.0 mL/min

The Headspace parameters (Agilent 7697A headspace auto sampler) are listed in **Table 3-2.**

Table 3-2: Headspace parameters

Temperatures	
Oven	70°C
Loop/valve	80°C
Transfer line	90°C
Times	
GC cycle time	15 min
Vial equilibration time	10 min
Pressure equilibration time	0.10 min
Inject time	0.50 min
Vials	
Fill mode	Flow to pressure
Fill pressure	15.00 psi
Fill flow	50.0 mL/min
Loop fill mode	Default
Loop fill ramp rate	00.0 mL/min
Loop final pressure	10.05 psi
Loop equilibration	0.05 min
Vent after extraction	Yes
Vial size	20 mL
Shaking	1
GC carrier control pressure	4.10 si

3.7.7.5 Running samples

The samples were loaded onto a headspace auto sampler. The sequence was in such a way that the first sample was the blank sample followed by the appropriate calibration standards. A verification standard then followed, after every tenth sample. Sufficient gas supply was ensured to complete a run.

3.7.7.6 Calculating THM formation potential

THMFP within a sample is calculated by subtracting the initial THM concentration from the final THM concentration (THM_f - THM_i). THM was measured after 30 minutes ($THM_{initial}$) of incubation and after the 7 day incubation period (THM_{final}). After the 7 day reaction period, the final chlorine residual of each sample was measured and the sample was quenched with ascorbic acid. Due to THM_i being close to zero and considered negligible, this value was not used in the THMFP calculation. THMFP is thus equated to the final THM concentration (THM_f), and is referred to as the THMFP of the sample.

3.8 NOM TREATABILITY ASSESSMENT

The core of this research study is based on the treatability assessment, which tracks the major NOM fractions from source water, through the treatment process and up to the final water produced by the RW full scale plants. The aim of the treatability study was to:

i.) Establish the effectiveness of the treatment process in terms of NOM removal over a period of various seasons (and years) and to determine the impact of NOM seasonality on THM formation in the final treated water.
ii.) Determine how the structure and character (fluorescence and polarity) of NOM changes during the water treatment process.
iii.) Identify the difficulty in removing the THM forming NOM fractions within Vaal Dam source by establishing the main fraction responsible for TTHM formation within the 4000 Ml/d utility.
iv.) Determine the relationship between degradation of liable DOC and heterotrophic bacteria present within the water treatment system, by establishing the NOM fraction that are more biodegradable.

In conclusion, the key objective of the treatability assessment is to identify the difficult to remove THM forming NOM fraction as well as the NOM fraction that has a high degradability by drinking water bacteria within the system. Henceforth a NOM characterization and monitoring protocol can be suggested to the bulk water service provider in South Africa to enhance removal of the specific NOM fraction. **Figure 3-5** is a schematic illustration of the NOM characterization and fractionation procedures and THM formation potential (NOM characterization and monitoring protocol), which aids in determining NOM treatability and identifying the problematic NOM fraction. Fractionation and characterization were performed on the source water and water sampled at the full scale plant after the coagulation/flocculation step.

The focus of the BDOC analysis was on Vaal Dam source water, with the aim to improve the 6 day BDOC analysis into a more rapid, less time consuming method. For the THMFP investigation, source water as well as treated water after sand filtration were sampled and chlorinated. This will determine the reduction of THMFP by the full scale WTP and identify the NOM fraction that is more prone to forming THMs after chlorination.

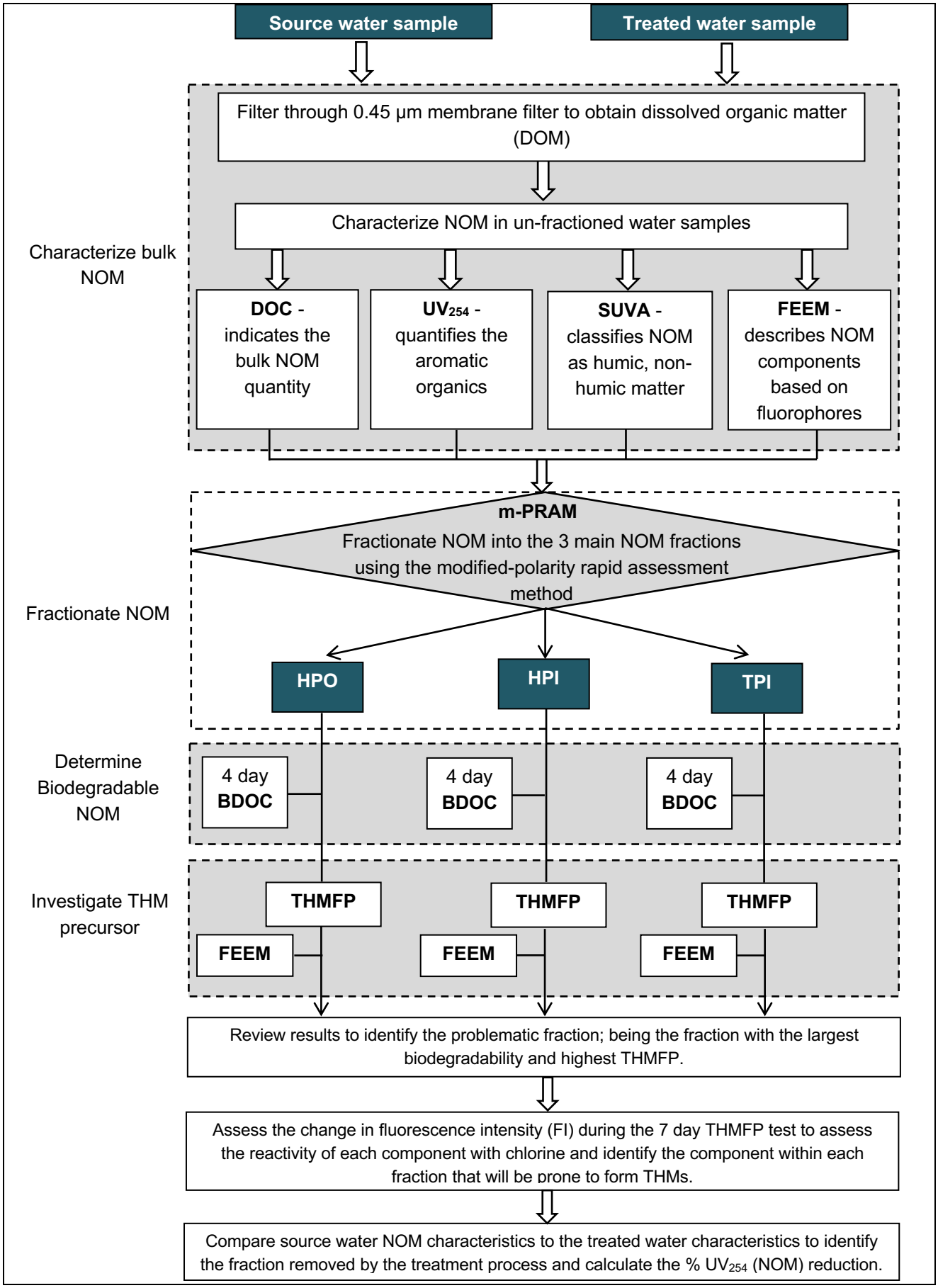

Figure 3-5: Schematic diagram of the NOM characterization and monitoring protocol

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CHAPTER 4: SEASONAL INFLUENCE OF NATURAL ORGANIC MATTER (NOM) CHARACTER AND PRECURSOR REMOVAL BY FULL SCALE CONVENTIONAL WATER TREATMENT

4.1 INTRODUCTION

Even though NOM monitoring and removal data for South African drinking water treatment plants is restricted, it has been established that the composition and quantity of organic matter throughout South African surface waters differs. This variable organic matter in the country results in high inconsistency in treatment plants using these surface waters (Nkambule *et al*., 2012).

Rand Water being the bulk drinking water service provider in South Africa, supplies an average of 4.2 million m^3/d potable water to 13 million people in South Africa and abstracts its source water from the Vaal Dam (storage capacity: 2536 million m^3 water). It is therefore critical to establish the quantity and quality of organic matter within this impoundment, including possible seasonal influence. Currently no historical data on NOM characterization exists for the Vaal Dam surface water. The outcome of the study will establish the nature and amount of NOM in Vaal Dam surface water, which is of great importance as the removal of NOM during drinking water treatment is prominently influenced by the quantity and quality of organic matter (Hu *et al*., 2003; Sharp *et al.,* 2006). To emphasize the importance of NOM monitoring during potable water treatment, this chapter evaluates the efficiency of NOM removal by a conventional drinking water treatment plant evaluating the influence of seasonal trends and organic loading during the removal of NOM.

The work presented in this chapter was published in Water Science and Technology: Water Supply 17.5, 1287-1297 (2017); DOI: 10.2166/WS.2017.028.

4.2 EXPERIMENTAL DESIGN

4.2.1 Full scale WTP plant seasonal sampling

The South African bulk water service provider utilise conventional water treatment with the following treatment steps: screening, coagulation, flocculation, sedimentation, carbonation, sand filtration followed by primary (chlorination) and secondary disinfection by addition of ammonia (chloramination) (Chapter 3 – **Figure 3-1**). Treated water was sampled after the filtration and disinfection steps at the full scale plant on a fortnightly basis, concentrating on the low flow and high flow seasons. The catchment area receives seasonal rain during November – February (summer) and is referred to as the high flow season; low flow season being winter and spring with minimal rainfall (June - October). Results for the period under investigation (June 2010 to February 2018) are presented in this chapter.

4.2.2 Seasonal NOM quantity and quality analyses

The NOM fractionation and characterization techniques utilised during this study period is described in **Chapter 3** (**Sections 3.3** and **3.4**). During the study, the seasonal influence on NOM quantity (organic loading) was investigated by making reference to DOC, UV_{254} and SUVA analyses. The quality (composition) of the organic matter within the source water and removal of NOM by full scale conventional water treatment was assessed by the modified-polarity rapid assessment method (m-PRAM) and high performance size exclusion chromatography (HPSEC) techniques.

4.3 RESULTS AND DISCUSSION

4.3.1 NOM fractionation and characterization

The Vaal Dam source water has a medium colour (19 CU - 168 CU), turbidity between 34 and 100 NTU, a high pH (6.5 to 8.8) and a conductivity ranging between 16 mS/m and 25 mS/m. Hardness of the water varies between 48 and 82 mg/L as $CaCO_3$, alkalinity between 60 and 88 mg/L as $CaCO_3$ and an average bromide concentration of 0.18 mg/L. The calculated SUVA value of a water sample indicates whether composition of organic matter is mainly comprised of non-humic matter, humic matter or a combination of both (Edzwald and Tobiason, 2010). The SUVA value of the source water collected at the inlet of the WTP ranges between 2 and 4 L/mg.m. According to Edzwald & Tobiason (2010) a SUVA value

within this range is indicative of humic and non-humic organic matter, having a mixed molecular weight distribution with a HPO and HPI character. The three NOM fractions were obtained using m-PRAM during October to February months and the change in hydrophobicity within the surface water during the different seasonal flows (low flow vs. high flow) was monitored. Results obtained from m-PRAM indicate an even distribution of the HPI and HPO fractions within the source water, based on the UV_{254} measurements of each fraction during the study period (**Figure 4-1**).

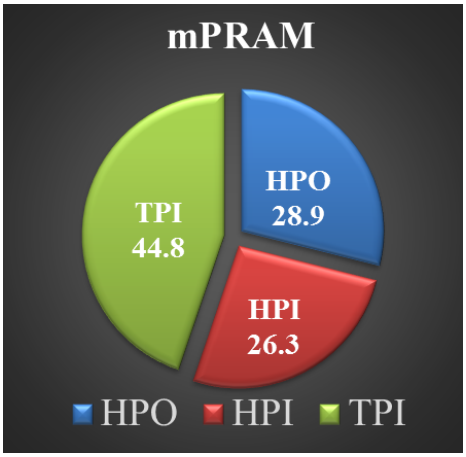
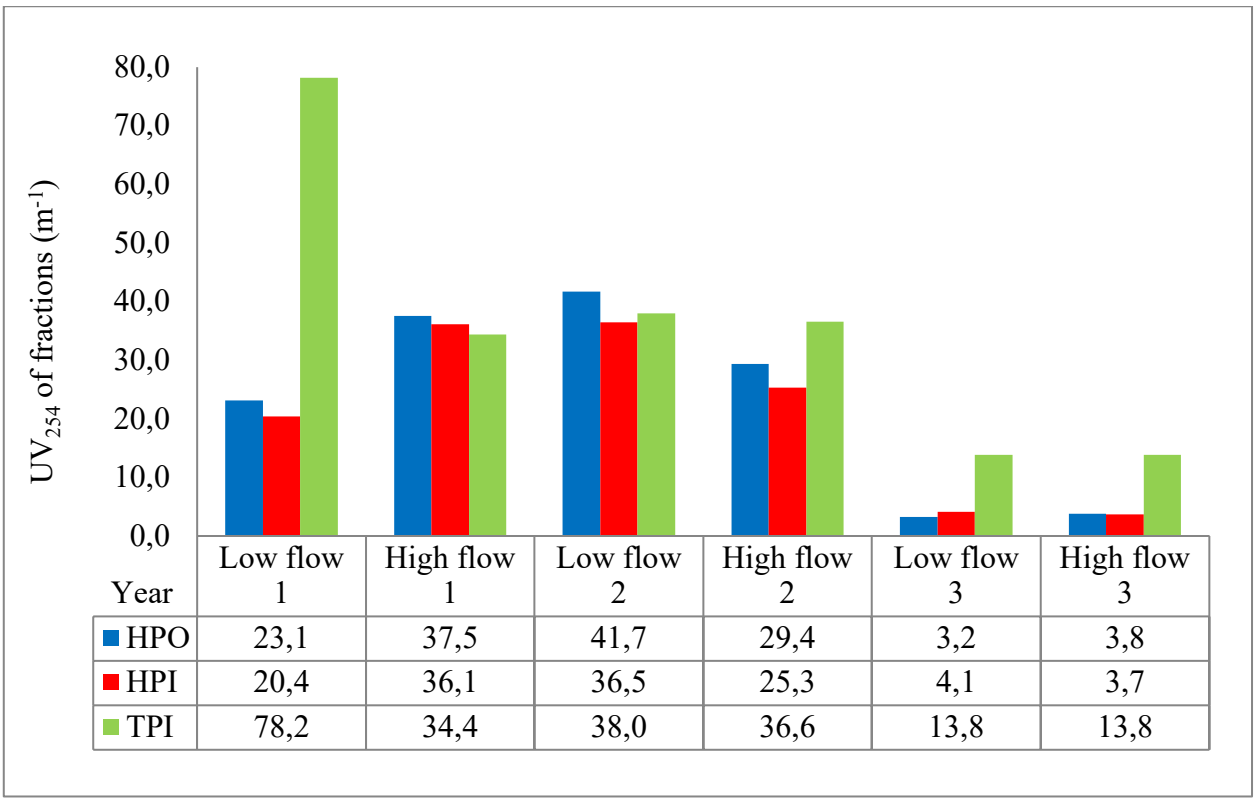


Figure 4-1: Percentage distribution of the HPO, HPI and TPI fractions within the source water

The distribution of the HPO, HPI and TPI fractions of the surface water during the high and low flow seasons is presented in **Figure 4-2**. Save for the high flow season of the first year (2010 to 2011) whereby a decrease in the TPI fraction was observed (from 78.2 m^{-1} to 34.4 m^{-1}), the distribution of the three NOM fractions within the raw water were in the order of TPI > HPO > HPI. Both the HPI and HPO fractions increased during the high flow season of the first year (2010 to 2011) possibly due to high terrestrial run-off within the Vaal Dam catchment area. According to Rosario-Ortiz *et al*. (2007) the negative charge of organic matter is represented by the NH_2 anion exchange filtrate, the TPI fraction. In general, the source water from the Vaal Dam has the ability of high anion exchange as indicated by the TPI fraction being the dominant organic matter fraction within the surface water during most of the seasons. During the study period under investigation, high seasonality was observed in the TPI fraction, as indicated by a UV_{254} of 78.2 m^{-1} within the first year compared to a UV_{254} of 13.8 m^{-1} in year 3, which indicates a variable NOM composition over the different years (**Figure 4-2**).



Year	Low flow 1	High flow 1	Low flow 2	High flow 2	Low flow 3	High flow 3
HPO	23,1	37,5	41,7	29,4	3,2	3,8
HPI	20,4	36,1	36,5	25,3	4,1	3,7
TPI	78,2	34,4	38,0	36,6	13,8	13,8

Figure 4-2: Annual and seasonal variation of HPO, HPI and TPI fractions obtained from m-PRAM

Whereas a decrease in the HPI and HPO fractions was evident during the high flow season of the second year (2011 to 2012), the polarity of the fractions was unaffected during the high flow season of year 3 (2012 to 2013). A comparative m-PRAM analysis of the low and high flow seasons of year 3 revealed an equal distribution of the HPI, TPI and HPO fractions. A possible explanation for the similar aromaticity observed in HPI, TPI and HPO fraction could be attributed to an early commencement in October of the rainfall period (October is regarded as a low flow season), which is indicated by an average rainfall of 234.0 mm in the low rainfall season (year 3) compared to 62.0 mm and 135.8 mm in the low flow seasons of years 1 and 2, respectively. Therefore, the m-PRAM results confirm the occurrence of seasonality in the character of organic matter, and this is evidenced by the variability in hydrophobicity during the various years. These results concur with those obtained by Bazrafshan *et al*. (2012), which suggested that the variation in NOM during different seasons does not follow a specific pattern.

4.3.2 Organic matter loading and removal by full scale conventional treatment

The bulk organic matter loading during the various seasons was quantified by DOC and UV_{254}. The efficiency of the WTP to remove NOM was also was quantified as the percentage reduction in UV_{254} and DOC after the various treatment steps. **Table 4-1** indicates that surface water DOC mostly increases when comparing the low flow season to the high flow seasons of the first four years and again in year 7. NOM removal attained by the conventional water treatment process and measured as DOC, also increased during the first four years and year 7 of the study period. Increases in DOC levels throughout the various seasons was also highlighted by Sharp *et al*. (2006) resulting in an increase in the DBP production. The average DOC levels during years 5, 6 and 8 showed a similar trend. To this end, DOC values, which were accompanied by lower DOC removal rates (measured at the full scale plant), were found to be lower during the high rainfall season. These results are in agreement with a study undertaken by Parsons *et al*. (2004) whereby increased DOC values were associated with increased percentage of post-treatment DOC removal.

SUVA has also been used in other studies to predict the reduction of NOM after coagulation (Parsons *et al.,* 2004; Edzwald & Tobiason, 2010). During the high flow seasons of all eight years of the study period, a decrease in SUVA was observed (**Table 4-1**). Large SUVA values indicate that humic substances are the prominent fraction within NOM and increased organic carbon removal can be anticipated by coagulation (Matilainen *et al*., 2005; Edzwald & Tobiason, 2010).

The aromatic character of NOM is measured by the light absorbed by organic matter at 254 nm wavelength; the double carbon bonds within the organic matter structure absorb UV light at this wavelength (Edzwald &Tobiason, 2010). Increased UV_{254} values indicate a large fraction of aromatic NOM exists and is indicative of NOM having an HPO character (Kitis *et al.,* 2002; Hassouna *et al*., 2014). Comparable studies have proven that HPO organic matter has a large SUVA value that is attributed to strong positive associations between SUVA and HPO NOM (White *et al*., 1997; Chowdhury, 2013). The likelihood that increased NOM (UV_{254}) removal percentages can be expected when large UV_{254} values within the source water is observed substantiates that the coagulation process favourably removes the HPO organic matter compared to the other NOM fractions.

Table 4-1: Seasonal and yearly averages of organic loading (DOC, UV_{254}, and SUVA) in the source water, with average percentage removal in brackets

Parameter / Period	DOC	UV_{254}	SUVA	Rainfall
	mg/L	m^{-1}	mg/L.m	mm
Year 1: 2010-2011	6.1*	98.3*	-	782.1*
Low flow	5.9 (22.1)	99.3 (87.3)	-	62.0
High flow	6.4 (22.0)	96.8 (85.4)	-	524.0
Year 2: 2011-2012	6.1*	40.2*	4.3*	522.0*
Low flow	5.7 (24.2)	74.0 (80.2)	5.2	135.8
High flow	6.4 (28.4)	28.0 (68.4)	4.2	316.0
Year 3: 2012-2013	4.7*	15.4*	3.2*	725.0*
Low flow	4.5 (20.1)	15.5 (51.2)	3.3	234.0
High flow	4.9 (25.3)	15.3 (62.1)	3.0	358.0
Year 4: 2013-2014	4.8*	17.5*	3.4*	490.0*
Low flow	4.4 (23.4)	16.3 (53.7)	3.5	85.0
High flow	4.8 (24.4)	18.5 (61.4)	3.4	282.0
Year 5: 2014-2015	5.8*	24.0*	4.4*	384.0*
Low flow	6.4 (21.7)	29.6 (56.8)	5.3	46.0
High flow	4.4 (15.7)	12.0 (34.2)	2.8	241.0
Year 6: 2015-2016	3.9*	15.9*	4.2*	355.0*
Low flow	4.1 (23.1)	14.9 (49.5)	4.0	41.0
High flow	3.9 (20.1)	16.5 (57.5)	4.2	228.0
Year 7: 2016-2017	3.3*	18.4*	4.8*	432.0*
Low flow	3.0 (32.6)	15.7 (69.5)	4.8	78.0
High flow	3.2 (39.2)	13.5 (61.7)	4.2	294.0
Year 8: 2017-2018	4.2*	35.4*	6.9*	272.6*
Low flow	4.7 (29.3)	37.0 (75.2)	6.6	45.0
High flow	3.6 (27.6)	33.3 (74.0)	7.6	227.6

* Mean of each year calculated from June – May.
Low flow: June – October; High flow: November – February.
Rainfall is the total rainfall during the various seasons and years.

As expected, corresponding decreases in the UV_{254} removal and SUVA values were observed during years 1, 2, 5 and 7 when the low and high flow seasons were compared (**Table 4-1**). During years 1 and 2, the percentage UV_{254} removal percentages decreased from 87.3% to 85.4% and 80.2% to 68.4%, respectively, when the low and high flow seasons were compared. Similarly, the average UV_{254} removal percentages also declined from 56.8% to 34.2% in year 5. For the third year, almost equal UV_{254} values (15.5 m^{-1} and 15.3

m^{-1}) were observed for the different rainfall seasons. From **Table 4-1**, it is evident that during year 3 and 4 SUVA values in the low flow and high flow seasons decreased from 3.3 L/mg.m to 3.0 L/mg.m in year 3 and slightly reduced from 3.5 L/mg.m to 3.4 L/mg.m during year 4.

This marginal difference between SUVA and UV_{254} in the source water during year 3 was accompanied by an increase in the percentage UV_{254} removal, which increased from 51.2% to 62.1% during the rainy season of year 3, and in year 4 increased from 20.1% to 25.3%. This proves that aromaticity (UV_{254} and SUVA) of source water is a useful parameter for monitoring efficacy of the treatment process in terms of organic matter removal. As shown in **Figure 4-3**, high raw water SUVA values often resulted in increased NOM removal (measured as UV_{254}). Raw water SUVA values above 5 L/mg.m resulted in NOM removal by the full scale conventional WTP and these ranged from 60 to 80% (**Figure 4-3**). This concept is supported by data emanating from this study, which suggest positive correlations between the source water UV_{254} and UV_{254} removal and also between source water SUVA and UV_{254} removal (**Figure 4-3**). These values forecast that source water with a high SUVA value will result in increased UV_{254} removal, which was also recognised at different water treatment plants (White *et al.,* 1997; Parsons *et al*., 2004).

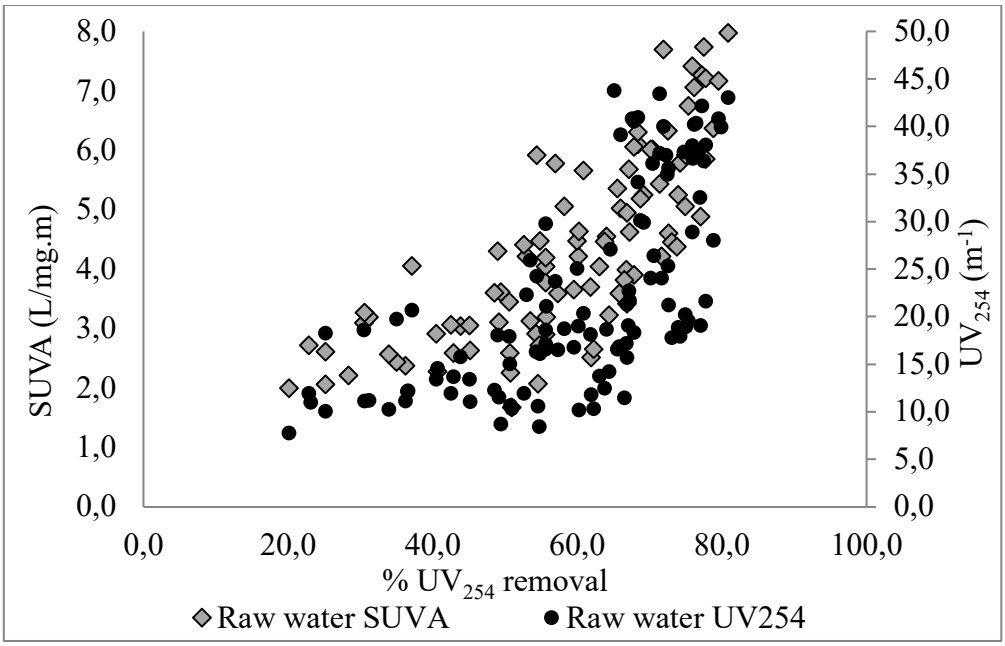


Figure 4-3: Positive associations between source water SUVA and UV_{254} removal and between UV_{254} of the source water and UV_{254} removal

From **Figure 4-3** it can be concluded that the SUVA value of the source water can be used to predict the percentage UV_{254} removal by the coagulation process. A one parameter model

for this prediction was developed from the full scale percentage UV_{254} removal data, using linear regression and is presented in **Equation 4.1**.

$$\%UV_{254}\ \text{removal} = 0.096 \times \text{source water SUVA} - 1.1819 \quad [4.1]$$

Figure 4-4 indicates the calculated percentage UV_{254} values versus the actual full scale percentage UV_{254} removal achieved. At a 95% prediction interval the Z-score was calculated as -0.08 using **Equation 4.2**.

$$Z = \frac{x - \mu}{\sigma} \quad [4.2]$$

Where Z = Z-score,

x = Predicted UV_{254} removal

μ = Mean actual UV_{254} removal

σ = Standard deviation of actual UV_{254} removal

This Z-score indicates that the predicted value is 0.08 standard deviations less than the actual mean value and the predicted percentage UV_{254} removal values are close to the mean UV_{254} removal observed after coagulation at the full scale WTP.

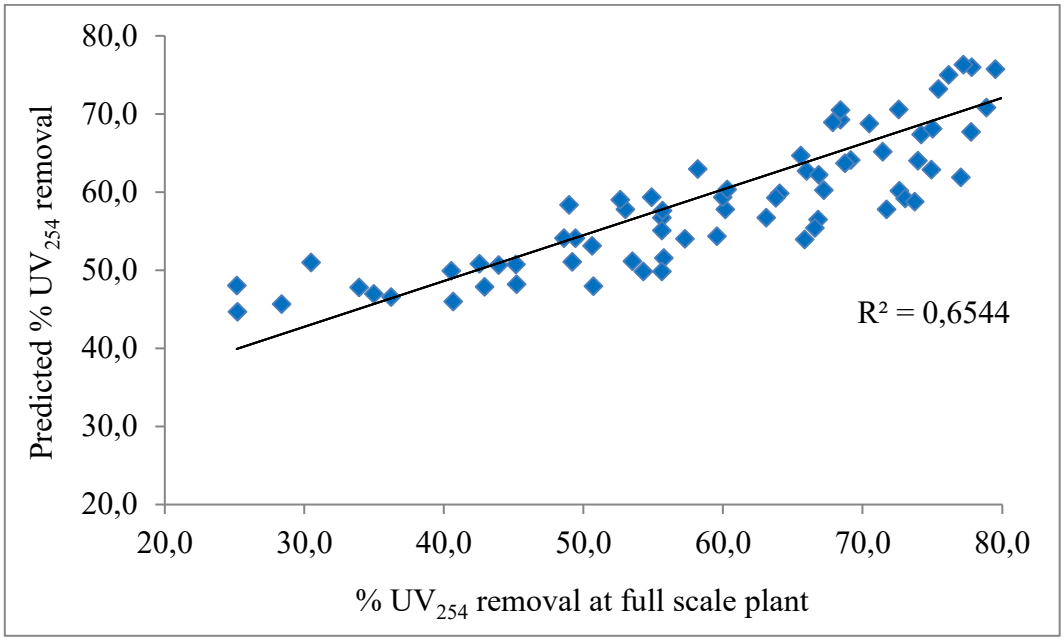


Figure 4-4: Predicted vs experimental % UV_{254} removal using a one parameter model with source water SUVA as predictor (Equation 4.1)

The average SUVA value of the treated water decreased from 1.8 L/mg.m in year 3 (low flow season) to 1.5 L/mg.m (high flow season). In year 6, the SUVA value also decreased during the low flow season from 1.9 L/mg.m to 1.5 L/mg.m during the high flow season,

whereas the final water SUVA remained unchanged in the final treated water in year 7 (1.5 L/mg.m). In summary, the average SUVA values after full scale treatment were below 2 L/mg.m during years 3, 6, 7 and 8, and decreased during the high flow seasons indicating good removal of aromatic NOM during the rainy summer months. Research undertaken by by Kitis *et al.* (2001) revealed that the SUVA value of final treated water are not easily reduced to below 1.5 L/mg.m when using conventional water treatment (coagulation). SUVA values of the treated water can therefore be useful when evaluating the effectiveness of the treatment process towards the removal of organic matter.

By making use of SUVA as a parameter to determine the treatability of NOM, it can be concluded that good removal of organic matter was accomplished since the aromatic HPO organic matter was more prominently removed by coagulation. An average NOM (UV_{254}) removal percentage of 65.5% was achieved during the eight year assessment. Studies where sand- and GAC-filtration was utilised revealed an organic matter removal percentage of 83% by sand filtration and 19% by GAC filtration (Nkambule *et al*., 2012). In a study performed by Chen *et al*. (2007) an organic matter removal of 36% was achieved by GAC filtration. However, poor correlations between aromatic NOM (SUVA and UV_{254}) and the various flow seasons were observed ($R^2 < 0.5$). Nevertheless a decreasing trend in the UV_{254} of source water, which was accompanied by smaller SUVA values and increased the formation of TTHM in the final treated water during summer (i.e. high flow season), was observed. Although the quantity of NOM varied during the high and low flow seasons, clear seasonality of NOM character was not evident and uniform throughout the period of investigation.

Characterization of NOM by HPSEC entails the separation of molecules based on their molecular size when they move through a gel matrix, and molecules larger than the pores located within the gel are eluted first (Nissinen *et al*., 2001). Efficiency of NOM removal by a WTP can be assessed using HPSEC analysis in order to compare and evaluate the molecular size distribution (MSD) in a sample before and after treatment (Matilainen *et al*., 2002). Five NOM fractions (indicated by peak height) are generally eluted when this technique is used. Whereas the high molecular weight (HMW) NOM are represented by peaks I and II, the intermediate molecular weight (IMW) fraction are denoted by peaks III and IV. The low molecular weight (LMW) fraction is on the other hand represented by peak V (Vuorio *et al*., 1998).

Figure 4-5 shows the typical molecular size distribution with the peak heights plotted against the time that the different fraction (e.g. HMW or LMW) was eluted. The unit of measure for the various peaks is milli absorbance units (mAU) and the elution time ranges from 0 to 20 minutes. An HPSEC chromatograph showing the various peaks is presented in **Figure 4-5**.

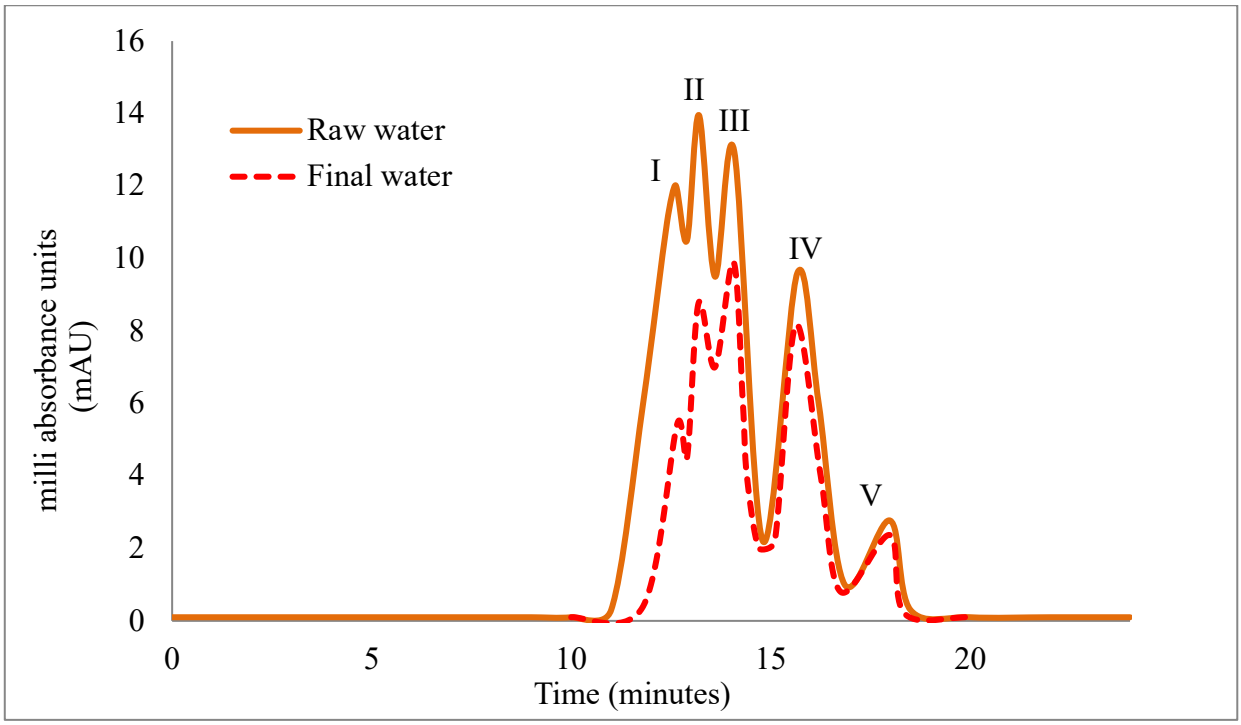


Figure 4-5: HPSEC chromatograph indicating the peak heights within the raw and final water

Figure 4-6 is the summative graph of data obtained from the chromatographs and illustrates a reduction of each molecular sized NOM fraction after sedimentation, rapid gravity sand filtration, and chlorination (primary disinfection) and chloramination (secondary disinfection) steps. The transformation of each molecular weight fraction after the various treatment steps is utilised to demonstrate the removal of these fractions after full scale treatment. According to the HPSEC results, the NOM comprised 51% HMW organic matter and an average of 45% of this fraction was reduced after treatment. The LMW weight fraction represented by peak V was unaffected and not removed by the water treatment process (**Figure 4-6**). These findings are in agreement with other studies, which suggest that coagulation is capable of reducing HMW organic matter and that the smaller molecular weight fractions are not affected by conventional water treatment (White *et al.*, 1997; Chiang *et al.*, 2002; Matilainen *et al.,* 2005). The LMW organic fraction is associated with non-humic NOM and the HMW NOM is indicative of humic and fulvic matter of terrestrial origin (Szabó & Tuhkanen, 2007).

A high percentage removal of the IMW and HMW organic matter is evident following the coagulation (sedimentation) step; this observation was corroborated by other investigations (Vuorio *et al.,* 1998; Matilainen *et al.* 2002). The reduction of the smaller molecular weight NOM (LMW) still remains a challenge due to the high charge of this fraction, which requires additional destabilisation during the coagulation and flocculation steps. Although the highest removal of HMW NOM was evident after sedimentation (due to coagulation), a further change in the molecular structure was observed after secondary disinfection. This is indicated by smaller milli absorbance units (mAU) of the HMW and IMW fractions of the water sampled at secondary disinfection compared to the water sampled after the sedimentation and filtration steps (**Figure 4-6**).

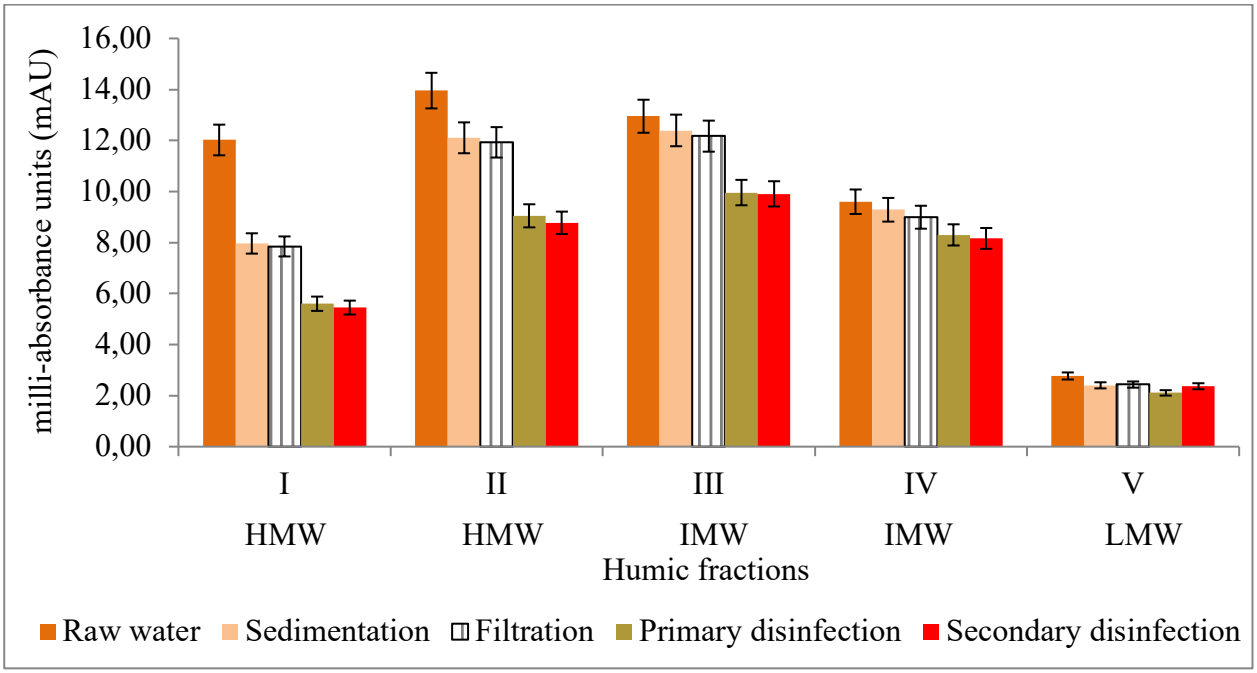


Figure 4-6: Change in molecular size distribution (MSD) measured by HPSEC after the various treatment steps

4.3.3 Formation of trihalomethanes (THMs) in final treated water

The DBPs formed during the chlorination step are primarily THMs, namely the four individual THMs known as dibromochloromethane (DBCM), bromodichloromethane (BDCM), bromoform and chloroform (Knight *et al.*, 2011; Kristiana *et al.*, 2011). The sum of these four compounds was reported as total THM (TTHM) with the detection limit of the individual compounds being 0.21 µg/L for chloroform, 0.36 µg/L for bromoform, and 0.27 µg/L and 0.33 µg/L for BDCM and DBCM, respectively. The THMs present in the treated water consisted of all four THMs with DBCM and BDCM frequently measuring below

the detection limit. In this study chloroform was the dominant THM, contributing 85% to the total THM concentration.

According to Chowdhury (2013), NOMs of larger molecular size (HMWs) are responsible for producing a chloroform concentration of up to 75% higher compared to the chloroform formation from the LMW organic matter. The smaller molecular weight NOMs are usually precursors of BDCM and DBCM (Chowdhury, 2013). According to the THM data gathered in this study, BDCM and DBCM formation was found to be below the detection limit and were not the major THM component. It is therefore likely that the THMs formed emanates from the residual HMW fraction that was not removed by the treatment plant. This was confirmed by previous studies that show that the LMW organic matter are responsible for brominated THM formation and the formation of brominated THM often decreases at increased NOM molecular weight (Hua & Reckhow, 2007).

It is known that molecular weight substantially influences specific classes of THMs formed and it is not only influenced by the hydrophobicity of NOM (Hu *et al*., 2003; Hua *et al*., 2015). Moreover, HPO organic matter is closely related to THM formation, as evidenced by a trihalomethane formation potential (THMFP) of 194 µg/mg from the HPO fraction (Chiang *et al*., 2002). Świetlik *et al.* (2004) has also suggested that the disinfectants are capable of decomposing HMW organic matter, indicating that these larger molecular weight organics are more reactive to the disinfectant. This demonstrates that the formation of THMs is susceptible to the presence of HPO HMW organic matter that was not adequately reduced by the treatment process.

The TTHM data for high and low flow seasons during the eight year period is summarised in **Figures 4-7** and **4-8** using box-and-whisker plots, whereby the mean value is represented by the line within the box and the upper and lower whiskers indicate the maxima and minima TTHM values. With the exception in year 5, an increase in the mean TTHM concentration was observed for all the years during the low flow (June - October) season as compared to the high flow (November - February) seasons.

A high variation and an increase in the mean TTHM values were evident during the high flow seasons of years 1 and 4 when floods occurred in the Vaal Dam catchment area (**Figure 4-7**).

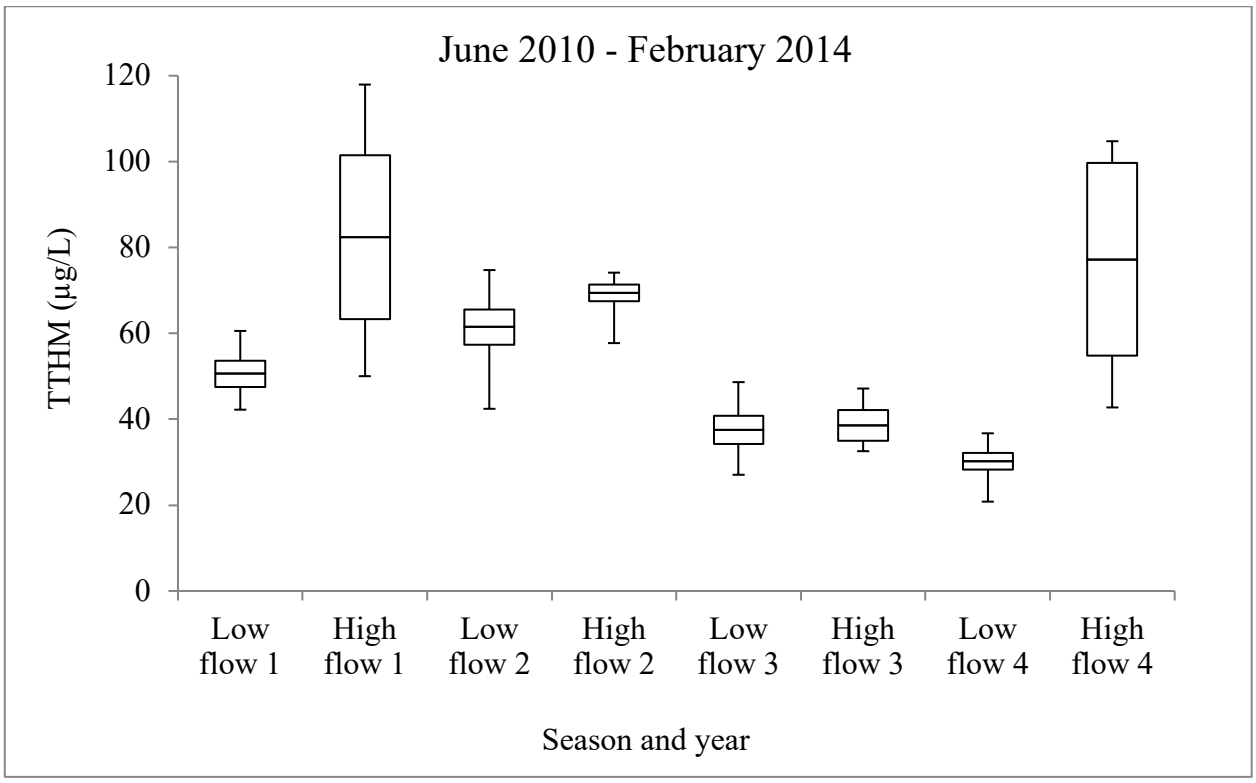


Figure 4-7: TTHM of the final treated water from 2010 to 2014 (n=118)

Year 1: 2010-2011; Year 2: 2011-2012; Year 3: 2012-2013; Year 4: 2013-2014; Year 5: 2014-2015; Year 6: 2015-2016; Year 7: 2016-2017; Year 8: 2017-2018; Low flow: June-Oct., High flow: Nov.-Feb.

The increased formation of TTHM in the treated water during high rainfall summer months was also observed in other studies (Knight *et al*., 2011; Golea *et al*., 2017). However, TTHM formation decreased from 60.8 µg/L during the low flow season to 42.9 µg/L during the rainy season in year 5 (**Figure 4-8**). During year 5 the average DOC of the source water decreased from 6.5 mg/L in the low flow season to 5.0 mg/L in the high flow season and year 5 experienced the lowest yearly average rainfall (31.9 mm), when compared with rainfall data of the other years.

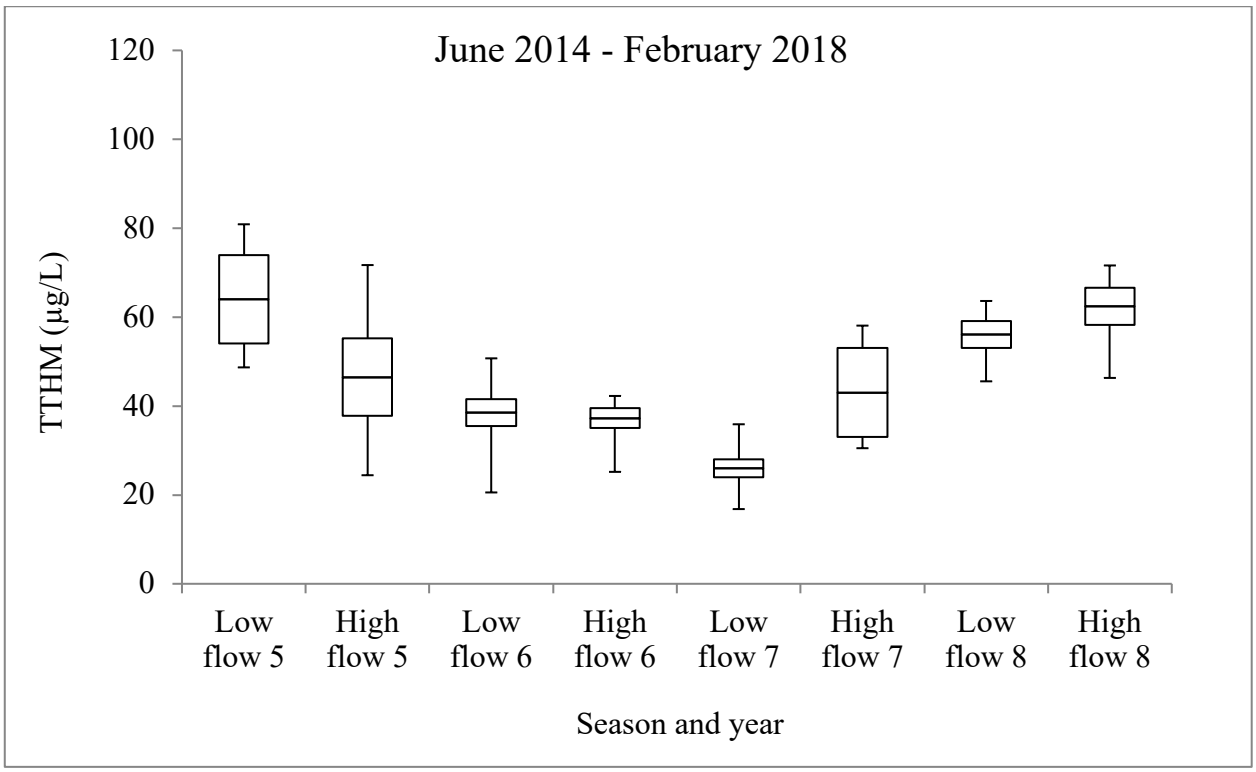


Figure 4-8: TTHM of the final treated water from 2014 to 2018 (n=109)
Year 1: 2010-2011; Year 2: 2011-2012; Year 3: 2012-2013; Year 4: 2013-2014; Year 5: 2014-2015; Year 6: 2015-2016; Year 7: 2016-2017; Year 8: 2017-2018; Low flow: June-Oct., High flow: Nov.- Feb.

During the study period, a definite relationship between aromatic NOM (SUVA and UV_{254}) and TTHM measured in the final drinking water in the distribution system was not established (**Figure 4-9**). Contradictory conclusions have been drawn where UV_{254} and SUVA were applied as a parameter to predict the formation of DBPs since a strong positive correlation was established between SUVA or UV_{254} and the formation potential of TTHM (Kitis *et al*., 2002; Hua *et al*., 2015; Golea *et al*., 2017). According to **Table 4-11** and **Figures 4-7** and **4-8**, a decrease in the removal of UV_{254} and an increase in the TTHM formation was observed during the high flow seasons of years 1, 2, 7 and 8. However, a poor correlation was observed between TTHM of the final treated water and UV_{254} of the source water as indicated by an R^2 of 0.1874 (**Figure 4-9**). This weak regression correlation between aromatic NOM character and the actual THMs formed indicates that aromatic organic matter is not the sole precursor to the TTHMs that were formed after the disinfection step. The occurrence of this phenomenon is also supported by Weishaar *et al.* (2003); NOM of low aromaticity was identified as a precursor for the formation THMs and raw water SUVA values poorly correlated with THMFP. Hua *et al.* (2015) also investigated the relationship between DBPs formed after the chlorination and chloramination steps and found a very poor correlation between TTHM and SUVA values after chlorination. To this end, correlation between chloraminated DBPs and SUVA was not established.

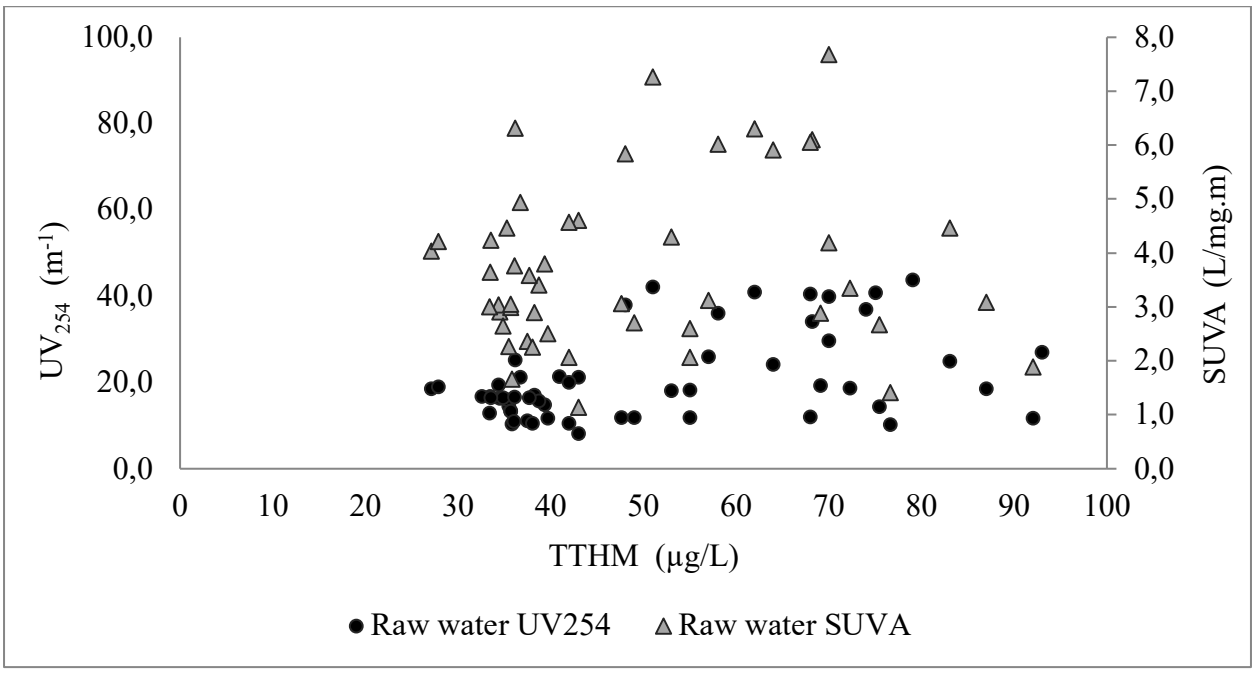


Figure 4-9: Weak association between aromatic constituents (UV_{254} and SUVA) in the source water vs. treated water TTHM

4.4 CONCLUSIONS

The novelty of the work presented in this chapter lies in the variability of organic matter characteristics within the Vaal Dam surface water, an oligotrophic water source. Although organic matter loading and the composition of NOM varies seasonally, a definite seasonal pattern cannot be predicted. A seasonal trend in NOM character (aromaticity) during the high and low flow seasons using Pearson's correlation was not evident. Nevertheless, seasonal impact on NOM quantity (amount) and quality (composition based on characteristics) was found to occur. The overall postulation here is that while the DOC of the source water increased during the high flow seasons (rainy summer months), a decrease in the corresponding aromaticity (SUVA) has led to an increase in the average formation of TTHM during the same period. The year 5 data did not however follow this trend.

Coagulation was found to be more effective towards the removal of aromatic HMW NOM compared to the non-aromatic LMW NOM. Overall, the average removal of NOM accomplished by the WTP was 65.5% and was in agreement with the treatability prediction tool (SUVA) for monitoring NOM composition within the surface water. It is reasonable to conclude that the SUVA value can be relied upon for predicting the removal of aromatic NOM by the full scale WTP, as high SUVA values (> 5 L/mg.m) will result in a NOM removal between 60 to 80%. As indicated in the literature, reduced UV_{254} removal percentages were

observed during episodes of low surface water SUVA values (< 4 L/mg.m), often during high flow seasons. Removal of NOM was not exclusively affected by the change in seasons (rainfall, temperature) but to a greater extent by bulk organic loading, since periods of increased UV_{254} or DOC values enhances the removal of organic matter.

A clear correlation between TTHM in the final treated water and raw water SUVA could not be established, therefore the amount of aromatic carbon could not be used to demonstrate NOM reactivity with chlorine. This indicates that aromatic humic components were not the sole precursor to the THMs that formed and thus suggests that non-humic non-aromatic compounds should also be acknowledged when investigating THM precursors. Also, when investigating the influence of the individual NOM fractions and their reactivity with chlorine, the THMFP method should be incorporated, instead of correlating NOM data with the actual THMs formed in the treated water.

The variability of NOM polarity during the various seasons and year that were investigated raises an awareness that characterization and NOM monitoring should occur on an on-going basis. This chapter also validates the importance of including unconventional (advanced) NOM characterization techniques during organic matter monitoring. This will inaugurate a sound perspective of the role that the individual NOM fractions play when the disinfectant is utilised at a water treatment plant. In the chapters to follow more emphasis will therefore be placed on establishing the relationship between the characteristics of the individual NOM fractions (HPO, HPI, TPI, molecular size of NOM) and their preference to form the individual THM species. The THMFP method will also be elaborated in order to to achieve this specific objective.

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CHAPTER 5: RELATIONSHIP BETWEEN CHARACTERISTICS OF NOM FRACTIONS AND THE FORMATION OF TRIHALOMETHANES (THMS)

5.1 INTRODUCTION

In order to enhance NOM removal and limit the formation of DBPs, it is however crucial to comprehend the character and reactivity of the major compounds responsible for the formation of DBPs. In South Africa, the only regulated DBP that is present in drinking water is in the form of THMs. Specifically, the individual forms of THMs that are regulated in South Africa are bromoform (100 µg/L), chloroform (300 µg/L), dibromochloromethane (DBCM) (100 µg/L) and bromodichloromethane (BDCM) (60 µg/L), and they are documented in the South African National Standard for drinking water (SANS 241:2015).

The structural composition (i.e. molecular size distribution), aromaticity and polarity of NOM vary within different geographical locations (Nissinen *et al*., 2001; Nkambule *et al*., 2012). Both the fluctuating character and quality of organic matter affects the removal efficiency of NOM and its reactivity with the disinfectant to form DBPs (Kitis *et al*., 2001; Roe *et al*., 2008; Lu *et al*., 2009). The treatability of NOM is affected by the composition of organic matter present within the source water (Parsons *et al*., 2004) and the aromaticity of NOM is often the leading contributor to THM formation (Kitis *et al*., 2001; Chowdhury & Champagne, 2008).

Although it is well known that NOM is the main precursor to DBPs, the molecular size of NOM is related to the amount of THMs formed during the chlorination step (Özdemir, 2014). The specific objective of this chapter is to determine the effect of NOM composition, specifically the molecular size distribution within the Vaal Dam surface water, on the formation of the four THMs generated at a chlorinated and chloraminated Water Treatment Plant (WTP).

The work presented in this chapter was submitted to the Journal of Water Process Engineering and is currently under review.

5.2 EXPERIMENTAL DESIGN

5.2.1 Water treatment plant (WTP) process train and sampling

At Rand Water the treatment steps consist of screening, coagulation, flocculation, sedimentation, carbonation, filtration followed by primary (chlorination) and secondary disinfection by addition of ammonia (chloramination). The chlorine dosage applied at primary disinfection is 3 to 4 mg/L. Surface water from the Vaal Dam was sampled at the intake of the full-scale water treatment plant. The water downstream of each of the treatment processes, as well as within the WTP process flow system, was sampled at the sampling points as indicated in **Figure 5-1**. After sampling at the selected sampling points, the samples were transported to the laboratory in a cooler box with ice packs, and the samples were refrigerated at 4 ºC until analysed. To measure the THMs present at the time of sampling, the residual chlorine of the treated water was reduced by adding ascorbic acid to the sample bottles. Surface and treated water samples were collected during a 12-month study period with a time interval of 14 days between each sampling run.

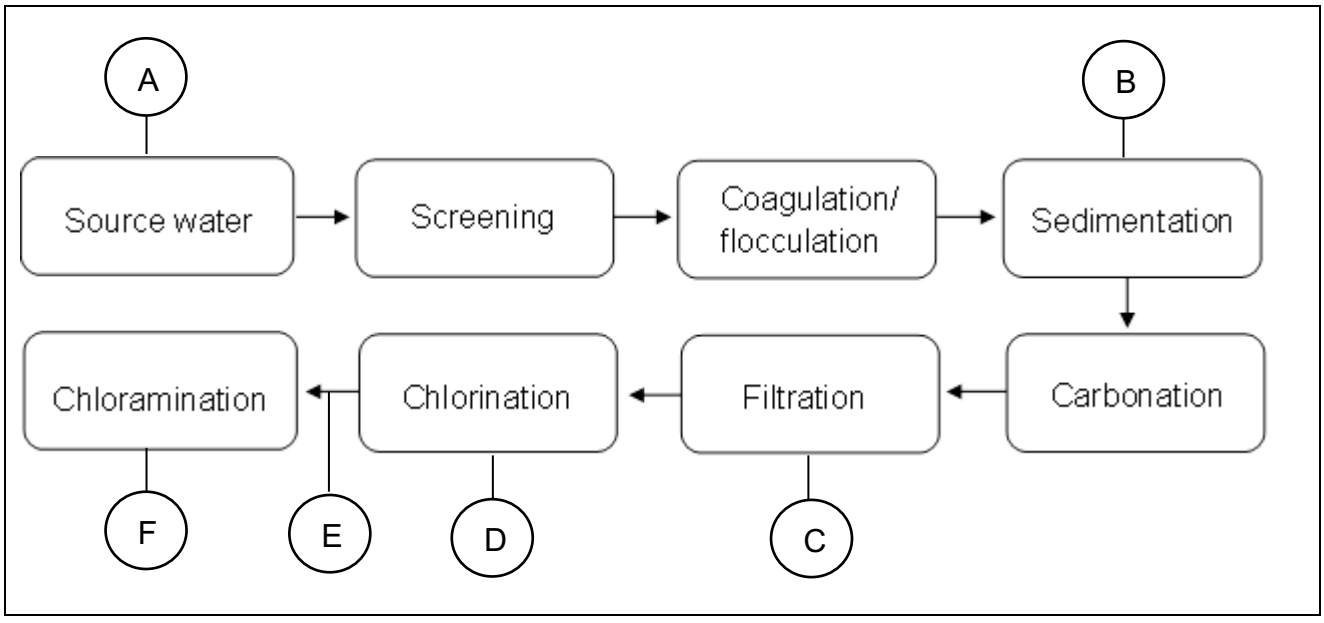


Figure 5-1: Rand Water treatment train and locality of the sampling points used during the experimental study

5.2.2 Source water characterization and trihalomethane (THM) analysis

Bulk organic content of the source water was investigated using DOC, UV_{254} and SUVA analyses, as described in **Section 3.3** of **Chapter 3**. To determine the correlation if any, between NOM molecular size and the formation of the individual THM species, high

performance size exclusion chromatography (HPSEC) was utilised (see **Chapter 3**). Removal of the organic matter after full scale treatment was also investigated using HPSEC to assess the change in the distribution of the molecular size of NOM after coagulation (sedimentation sampling point). THM analyses of the treated water of the three sampling points (D, E and F - **Figure 5-1**) were done according to the methodology described in **Chapter 3** (**Section 3.7.7**).

Water samples for THM analysis were collected downstream of the treatment processes, that is, immediately post-chlorination at the primary disinfection plant, as well as of the flow passing between the chlorination and chloramination stages, and immediately post-chloramination at the Secondary Disinfection Plant, as indicated by sampling points D, E and F, respectively, in **Figure 5-1**. Solid-phase extraction and a Headspace Sampler (Agilent 7697A) coupled to a gas chromatograph (Agilent 6890N) were used to analyse the water samples collected after the final water treatment stage, namely disinfection. The THMs in the samples were separated using a capillary gas chromatography column (J & W Scientific, 30 mm x 0.530 mm x 0.5 µm), followed by detection using an electron capture detector (ECD). Quantification of bromoform, chloroform, DBCM and BDCM formed part of the THM analyses. The detection limits were as follows: BDCM 0.27 µg/L, DBCM 0.33 µg/L, bromoform 0.36 µg/L and chloroform 0.21 µg/L.

5.3 RESULTS AND DISCUSSION

5.3.1 Source water characterization and organic matter removal

The source water had an average UV_{254} value of 24.3 m^{-1}, DOC of 5.70 mg/L, SUVA of 4.10 L/mg.m and a medium colour (see **Table 5-1**). The molecular size distribution (MSD) of the organic matter was determined using HPSEC, which produced various peak heights (**Figure 5-2**). Each of the HPSEC peaks represents a NOM fraction according to the order in which the peaks are formed. Six Peaks (I, II, III, IV, V and VI) were eluted, with the first peak being Peak I. Peaks I and II represents high molecular weight (HMW) NOM, Peaks III and IV the intermediate molecular weight (IMW) and low molecular weight NOM being represented by Peaks V and VI (Vuorio *et al*., 1998; Nissinen *et al*., 2001). Previous studies on the effect of NOM on THM formation suggest that HMW NOM is characterized by a molecular weight bigger than 30 kDa, while the LMW fraction has a size smaller than 1 kDa (Pelekani *et al*., 1999; Özdemir *et al*., 2014). In a study performed by Chowdhury & Champagne (2008), the

molecular weight of the organic matter ranged between 3 kDa and 500 Da for surface water samples having a DOC of 5.9 mg/L.

Table 5-1: Source water classification

Parameter	Unit	Mean	Min.	Max.
UV_{254}	m^{-1}	24.3	10.2	42.1
SUVA	L/mg·m	4.10	2.40	6.30
DOC	mg/L	5.70	4.10	8.30
TOC	mg/L	7.20	4.60	8.80
Humic acids	mg/L	5.90	3.40	7.60
pH	-	7.60	6.90	7.90
Colour	CU	89.6	41.0	116
Conductivity	mS/m	18.8	17.0	21.0
Turbidity	NTU	70.4	57.0	98.0
Alkalinity	mg/L as $CaCO_3$	70.0	60.0	88.0
Hardness	mg/L as $CaCO_3$	63.8	48.0	82.0
Bromide	mg/L	0.18	0.10	0.25

The MSD evaluation of the water samples following the sedimentation and disinfection steps, which represent a typical MSD observed during full scale treatment, are shown in **Figure 5-2**. The NOM fraction that was more readily removed was the organic matter of HMW, which is indicated by a greater reduction of Peak I as compared to Peak V (LMW NOM). It is evident from a comparative analysis of the raw water sample and the water sampled after the secondary disinfection (see **Figure 5-2**) that the quantity of the LMW organic matter remained constant during treatment; this is depicted by similar peak heights (Peaks V) that were recorded for both samples. The distribution of the molecular sizes observed in this study is comparable to those of other studies where the bigger molecular weight organic matter (> 3 kDa) tends to be selectively removed by the coagulation process (Parsons *et al*., 2004). The selective removal of bigger molecular weight organic matter was also confirmed by studies by Matailainen *et al*. (2002), which reported that LMW organic matter was not being removed by coagulation and LMW organics smaller than 1 kDa were thought to be the major precursor of DBPs (Özdemir, 2014).

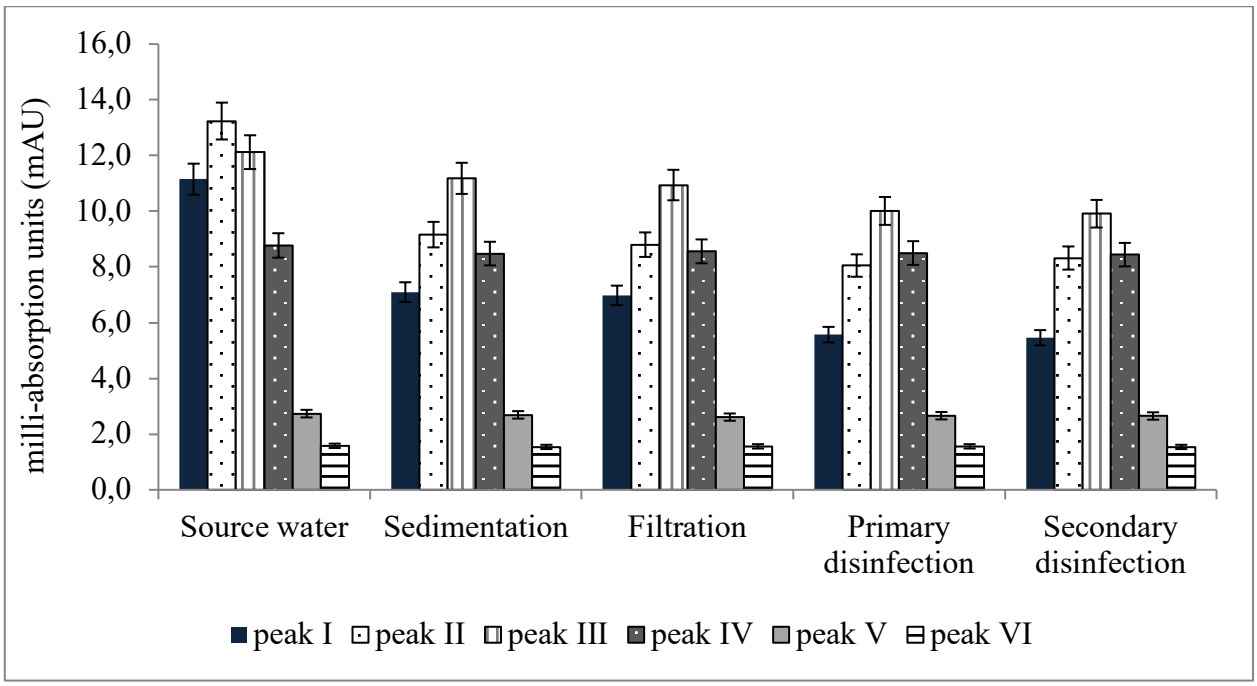


Figure 5-2: Average MSD of NOM after full-scale treatment, including standard error bars

Table 5-2 presents the height of the peak areas obtained from HPSEC analysis, with percentage of the total area Data from the HPSEC analysis indicating peak heights and the percentage of the total area of each fraction is presented in **Table 5-2**. In Vaal Dam source water the HMW fractions Peaks I and II dominated (**Table 5-2**, **Figure 5-2**). The percentages of Peaks I and II were on average 22.5% and 26.7%, respectively of the total area of NOM fractions in source water (**Table 5-2**). When comparing the percentage distribution of the individual fractions of the source water to the treated water (secondary disinfection), it is clear that Peaks I and II (HMW NOM) were mostly removed by the WTP (**Table 5-2**).

Table 5-2: Height of peak areas obtained from HPSEC analysis, with percentage of each fraction of the total area in brackets

	Peak height (% of total area in brackets) (mAU)					
	I	II	III	IV	V	VI
Source water	11.2 (22.5)	13.2 (26.7)	12.1 (24.4)	8.8 (17.7)	2.7 (5.5)	1.6 (3.2)
Sedimentation	7.1 (17.7)	9.2 (22.8)	11.2 (27.8)	8.5 (21.1)	2.7 (6.7)	1.5 (3.8)
Filtration	7.0 (17.7)	8.8 (22.3)	10.9 (27.7)	8.6 (21.7)	2.6 (6.6)	1.6 (4.0)
Primary Disinfection	5.6 (15.3)	8.1 (22.1)	10.0 (27.5)	8.5 (23.4)	2.7 (7.3)	1.6 (4.3)
Secondary Disinfection	5.5 (15.0)	8.3 (22.9)	9.9 (27.3)	8.4 (23.2)	2.7 (7.3)	1.5 (4.2)

The percentage of each fraction removed after the various treatment steps was calculated using the peak heights shown in **Table 5-2** and the subsequent percentage of each fraction remaining after treatment (sedimentation and filtration) is illustrated in **Figure 5-3**. The percentage HMW NOM (Peaks I and II) remaining in the water after sedimentation/filtration was observed to be, on average, 63.1% and 67.8% during the study period (**Figure 5-3**). It can be concluded that only a selective percentage of the high-molecular-weight humic acid fractions is removed by the treatment processes in this water treatment plant. A further decrease is also observed in Peaks I to III (HMW and IMW NOM) post-disinfection as compared to Peaks IV to VI (**Figure 5-3**). This additional reduction of HMW NOM was observed post-chlorination, indicating the reactivity of HMW NOM with chlorine.

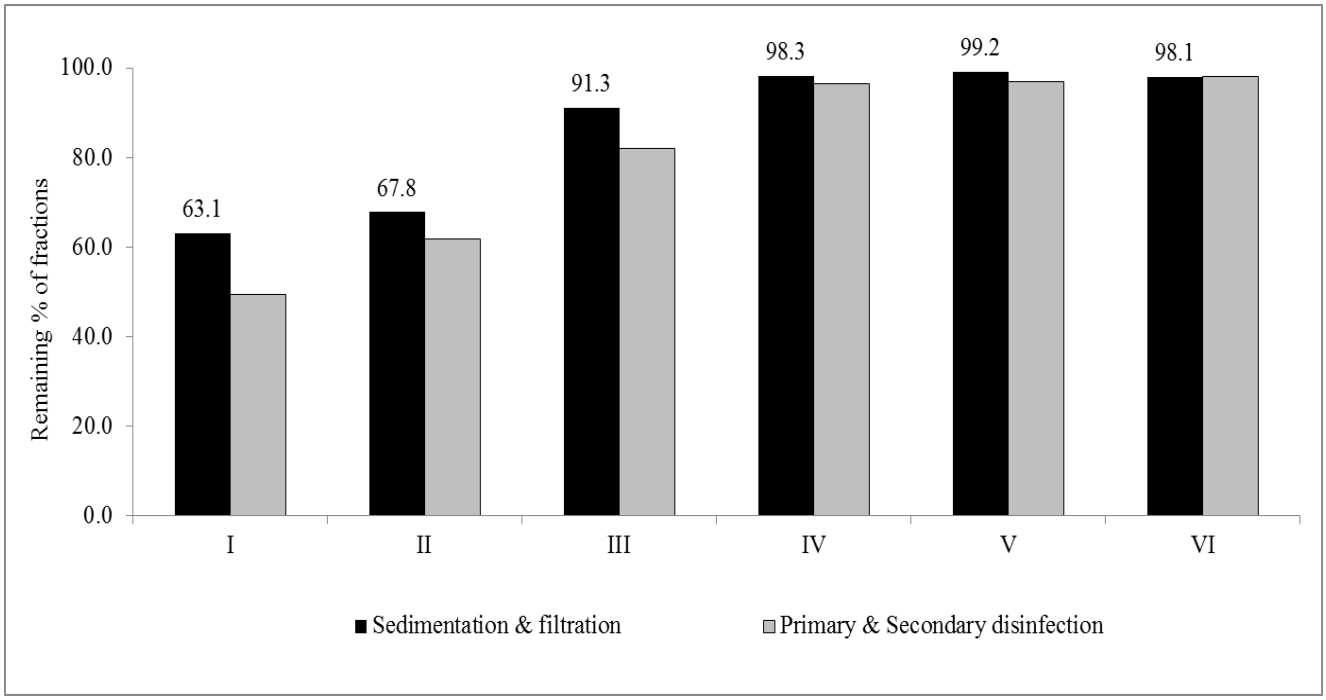
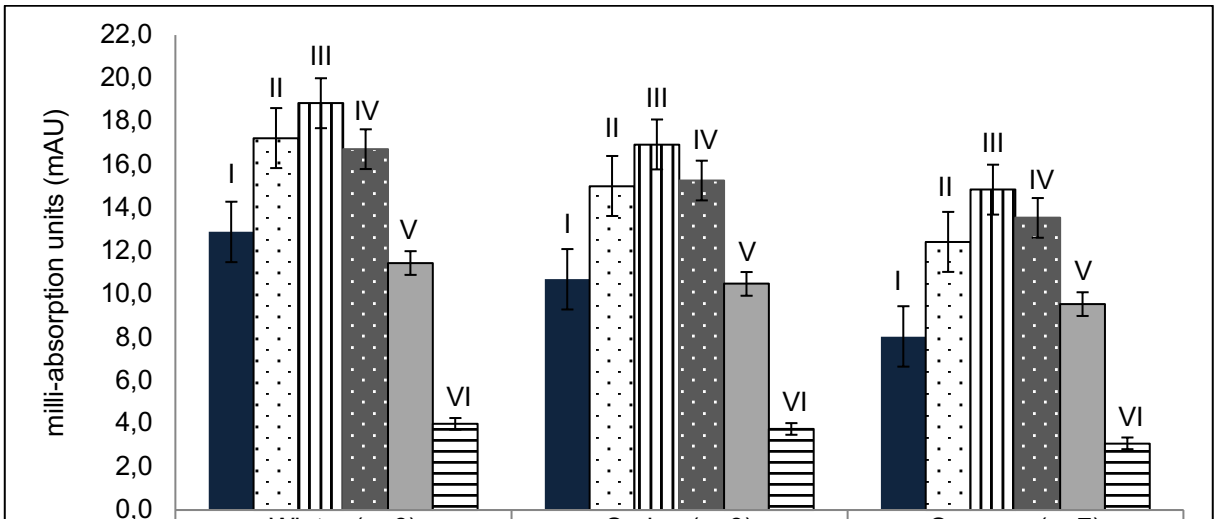


Figure 5-3: Average remaining percentage of fractions (Peaks I to VI) after full-scale treatment

The seasonal variability of the MSD of NOM within the source water is presented in **Figure 5-4**. A slight variation can be observed in the MSD data of the NOM during the four seasons. Such a variation in the composition of NOM in the surface water during the different seasons is not surprising and has been observed in other studies (Goslan, 2003; Sharp *et al*., 2006). A decrease in the total organic content during summer, which is indicated by a decline in the height of the various peaks (Peaks I to VI), was observed.

A similar seasonal distribution of the molecular weights was observed in the source water analysed by Matilainen et al. (2002) and Szabó & Tuhkanen (2007). To this end, an increase in the total organic content towards the winter months and lowest levels of the fractions during summer were recorded (Matilainen *et al*., 2002; Szabó & Tuhkanen, 2007). According to **Figures 5-3** and **5-4**, it can be seen that the unremoved LMW fraction (Peaks V and VI) decreases in the source water as summer approaches.



	Winter (n=6)	Spring (n=8)	Summer (n=7)
peak I	12,9	10,7	8,0
peak II	17,2	15,0	12,4
peak III	18,8	16,9	14,8
peak IV	16,7	15,3	13,5
peak V	11,4	10,5	9,5
peak VI	4,0	3,8	3,1

Figure 5-4: Seasonal variability of NOM MSD indicated by decreasing peak heights

5.3.2 Effect of organic matter molecular size on formation of individual trihalomethane (THM) species

It has already been established that a change in the MSD following treatment of NOM by a suite of treatment processes gives an indication of the effectiveness of that particular process towards the treatment of NOM (Vuorio *et al*., 1998; Matilainen *et al*., 2002). A question that now requires attention is whether MSD data can also be used to determine the molecular weight fraction that contributes to the formation of THMs. Apart from the size distribution of NOM that revealed variability during the different seasons, a positive correlation between HMW organic matter of the source water and TTHM formation was observed. Data relating to the individual molecular weight fractions (see **Figures 5-5** and **5-6**) seem to portray a very strong and positive correlation between Peaks I and II (HMW)

and the formation of chloroform, as calculated by $R^2 = 0.9633$ ($p < 0.05$) and $R^2 = 0.9501$ ($p < 0.05$), respectively. Given that the p-value that is below 0.05, these correlations are statistically significant.

The link of the HMW organic matter as the main precursor to THM formation has also been established in other studies; as reflected by a direct relationship between chloroform formation and HMW NOM of the relevant the source water (Chowdhury, 2013; Zhang *et al*., 2016). A reasonable correlation between HMW organic matter (Peaks I and II) and chloroform formation during winter months, which was supported by the respective correlation coefficient values of 0.5872 ($p < 0.05$) and 0.6930 ($p < 0.05$) (**Figures 5.5** and **5.6**), has also been established. More definite and stronger correlations were observed between larger molecular sized NOM and THMs formed in the final water sample during the warmer summer months. These correlations suggest that TTHM formation, more specifically chloroform formation, is highly influenced by the presence of HMW NOM in the source water (**Figures 5-5** to **5-7**). **Figure 5-8** depicts a moderate correlation between the HMW fractions of NOM and the formation of TTHM during the winter months ($R^2 = 0.6084$, $p < 0.05$). Such results have also been confirmed by other research investigations, which have demonstrated HMW hydrophobic NOM as the leading precursor in the formation of chloroform (Roe *et al*., 2008; Lu *et al*., 2009).

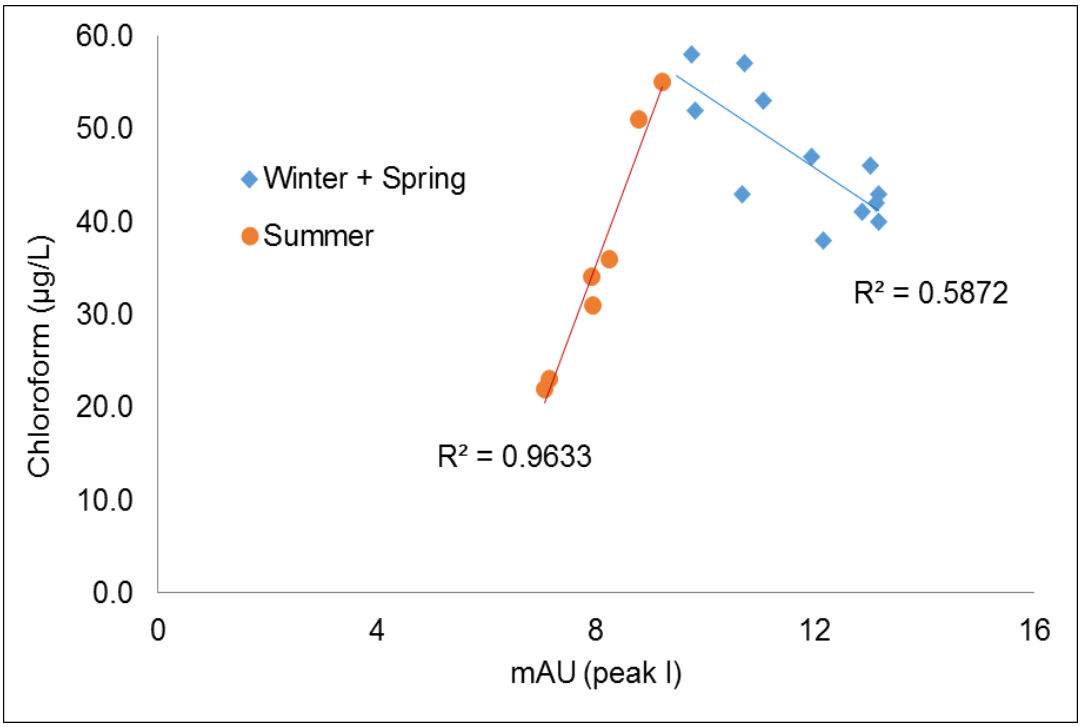


Figure 5-5: Seasonal correlation between peak I (HMW) and chloroform formation

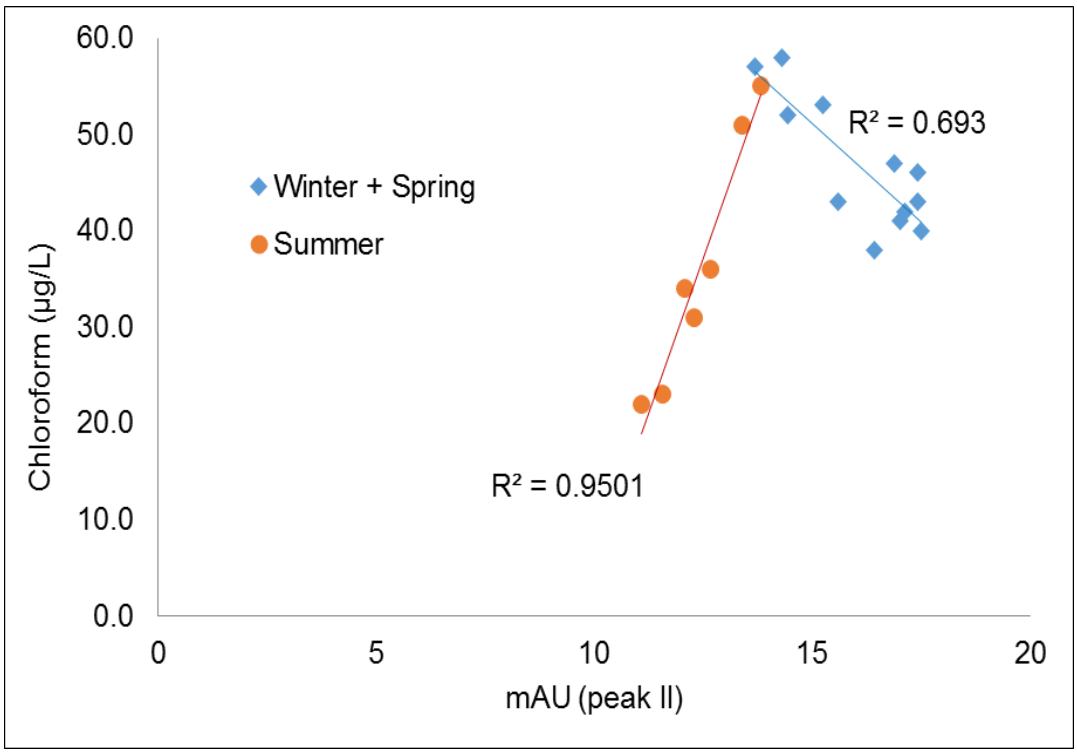


Figure 5-6: Seasonal correlation between peak II (HMW) and chloroform formation

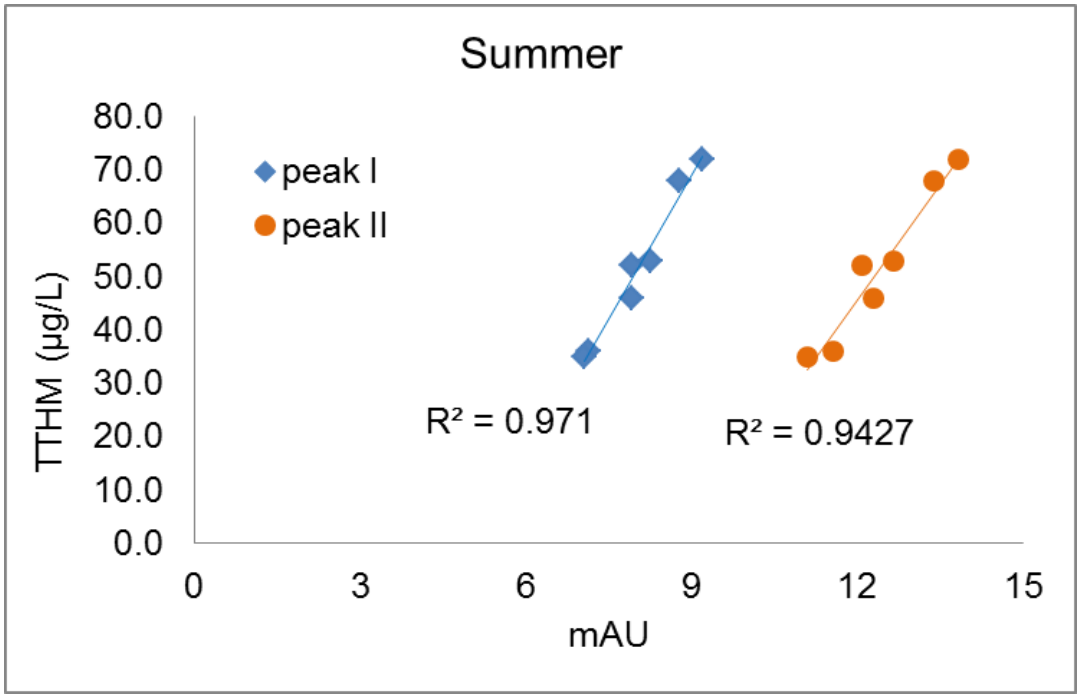


Figure 5-7: Positive correlation between HMW NOM and TTHM during summer

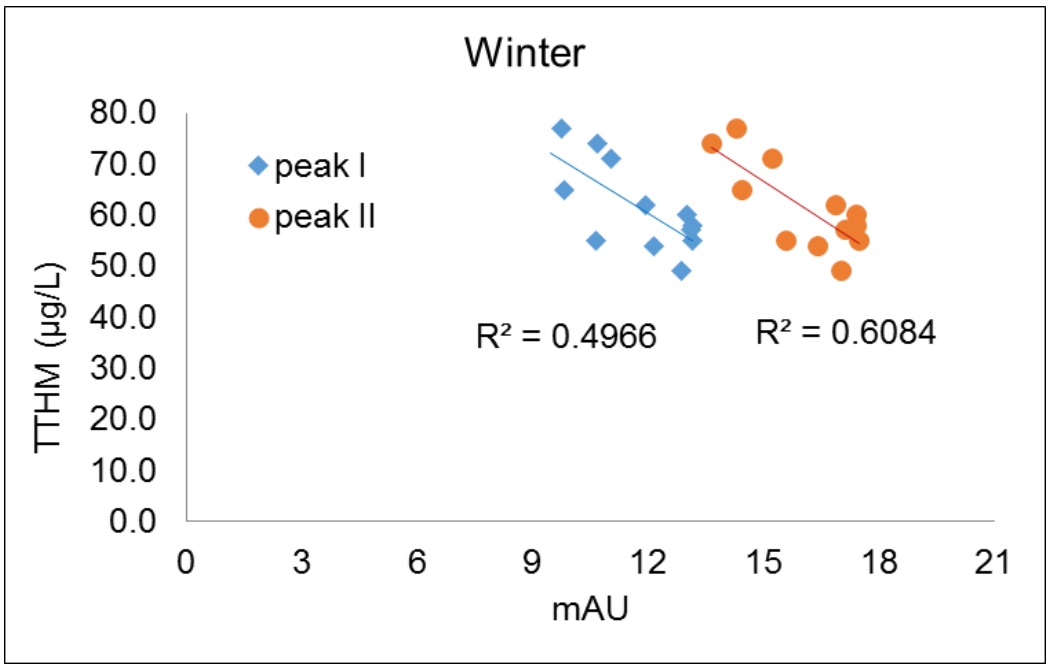


Figure 5-8: Moderate correlation between HMW NOM and TTHM during winter

It can be noticed from **Figure 5-9** that a reasonable correlation was found to exist between Peak IV (IMW NOM) and the amount of THM formed during winter, as indicated by a regression coefficient of 0.656 ($p < 0.05$). The correlation between chloroform and Peak V (LMW NOM) during winter was also moderate ($R^2 = 0.5887$, $p < 0.05$) (**Figure 5-10**). During summer, weak associations were apparent between the intermediate and smaller molecular weight organics and chloroform, judging by the correlation coefficients in the region of 0.259 (**Figures 5-9** and **5-10**). High molecular weight organic matter is strongly correlated with UV_{254} and SUVA (Edzwald & Tobiason, 2010; Chowdhury, 2013). Lower molecular weight fractions are often associated with low SUVA values (<2 L/mg·m) (Lu *et al.*, 2009; Özdemir, 2014).

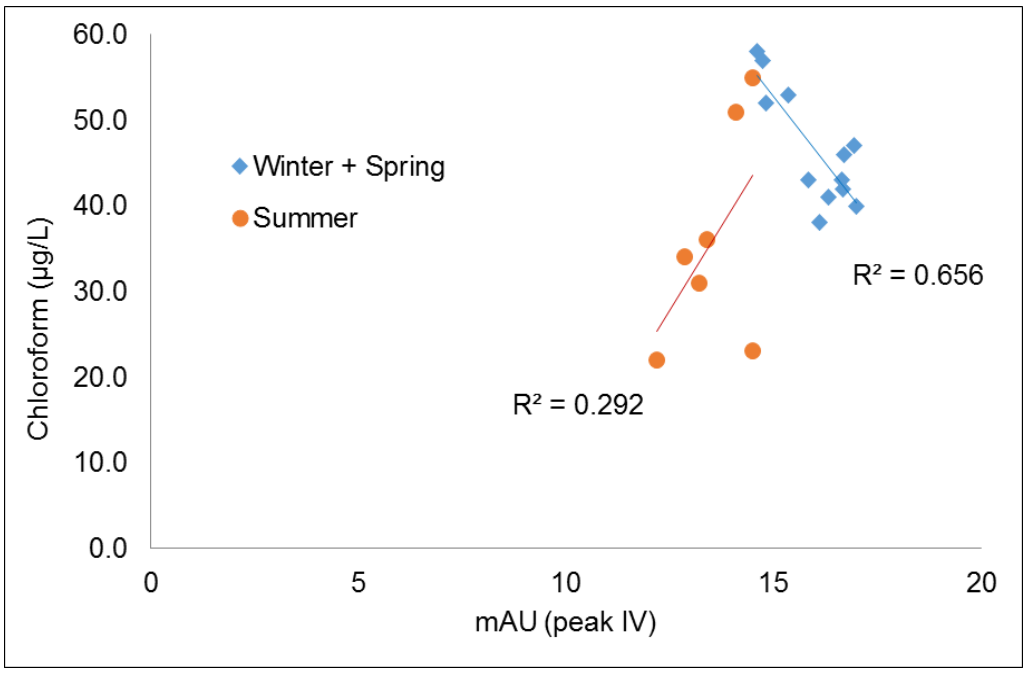


Figure 5-9: Seasonal correlation between Peak IV (IMW) and chloroform formation

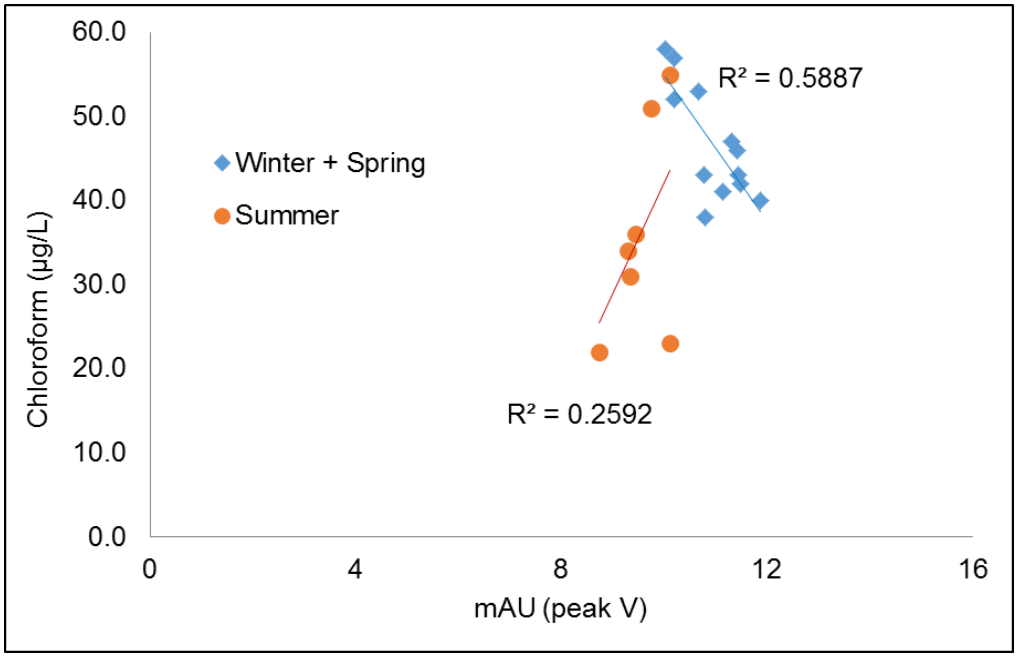


Figure 5-10: Seasonal correlation between Peak V (LMW) and chloroform formation

During summer (November to February) a stronger correlation was noted between the percentage UV_{254} removed and source water SUVA (**Figure 5-11**: $R^2 = 0.9369$; $p < 0.05$). The aromatic quantity of NOM (UV_{254}) correlated well with the UV_{254} percentage removal during both summer and winter seasons (**Figures 5-11** and **5-12**). This proves that

increased aromaticity of NOM in the source water results in increased NOM removal using full scale treatment.

However, no correlation was observed between aromatic NOM (SUVA or UV_{254}) and the THMs formed during the study period. It can therefore be concluded that UV absorbing properties of organic matter are not the sole precursor that contribute to the formation of THMs in the final treated water. Similar conclusions have been drawn from other studies, which suggest that SUVA is a weak indicator of THM formation (Fram *et al*., 1999; Weishaar, 2003; Hua *et al*., 2015). However, strong correlations were noticed between trihalomethane formation potential (THMFP) and aromatic NOM (and DOC) when the relationship between NOM character and treatability of the organic matter was investigated (Parsons *et al*., 2004; Van Leeuwen *et al*., 2005; Golea *et al*., 2017).

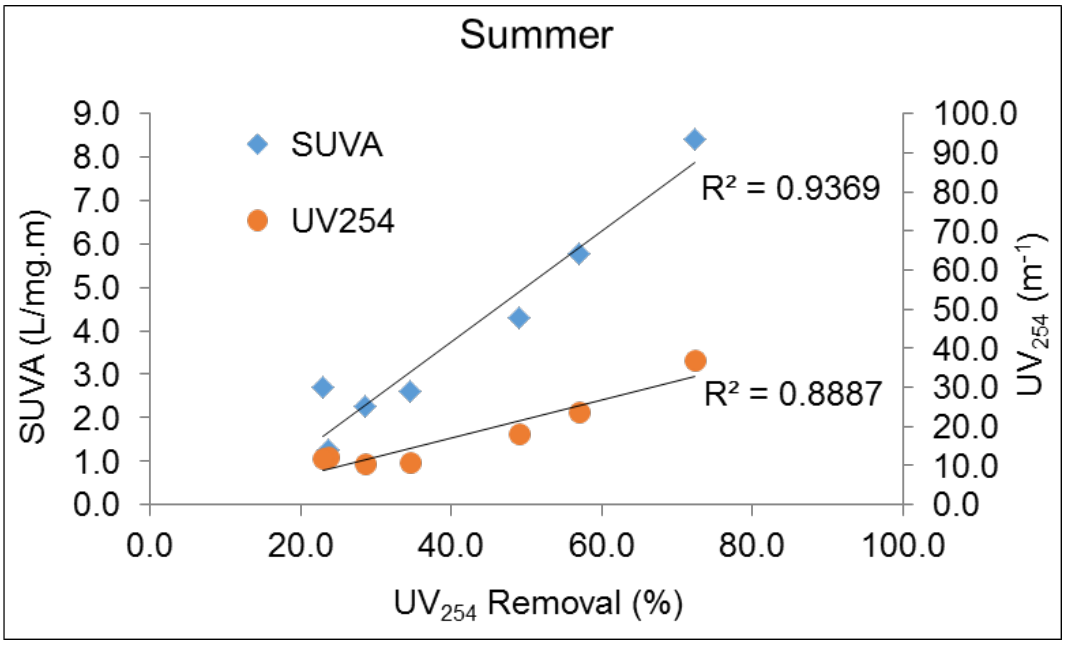


Figure 5-11: Correlations between source water SUVA and UV_{254} vs. UV_{254} percentage removal by the full-scale plant in summer

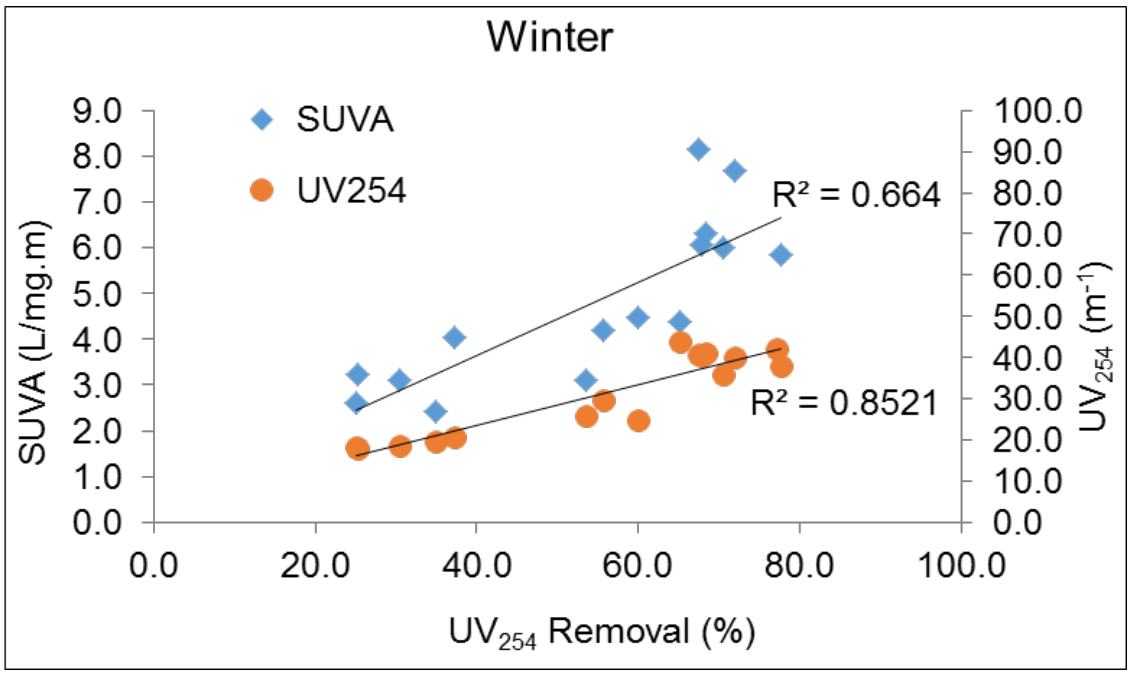


Figure 5-12: Correlations between raw water SUVA and UV_{254} against UV_{254} percentage removal by the full-scale plant in winter

5.3.3 Trihalomethane (THM) speciation and spatial variability of THMs

Chloroform, bromoform, dibromochloromethane (DBCM) and bromodichloromethane (BDCM) were quantified in the treated water samples and their sum total concentration was reported as total trihalomethane (TTHM) in µg/L. The detection limits for bromoform was 0.36 µg/L, 0.21 µg/L for chloroform, 0.33 µg/L and 0.27 µg/L for DBCM and BDCM, respectively. Bromoform and DBCM measurements are below the detection limit and are therefore not presented in the relevant graphs. Formation of brominated THMs (i.e. DBCM and bromoform) was expected due to the presence of a small bromide concentration in the source water (Lu *et al*., 2009; Ramavandi *et al*., 2015).

After chlorination (primary disinfection), the chloroform concentration constituted 67.2% of the total THM yield compared to 76.2% after secondary disinfection (i.e. chloramination). BDCM concentrations after primary and secondary disinfection were found to be 32.4% and 22.5% of the total THM concentration, respectively (**Figure 5-13**). This partitioning of THM formation concurs with data published in other research studies where chloroform and BDCM were documented as the two major THM species formed during chlorination/chloramination (Knight *et al*., 2011; Chowdhury, 2013; O'Driscoll *et al*., 2018).

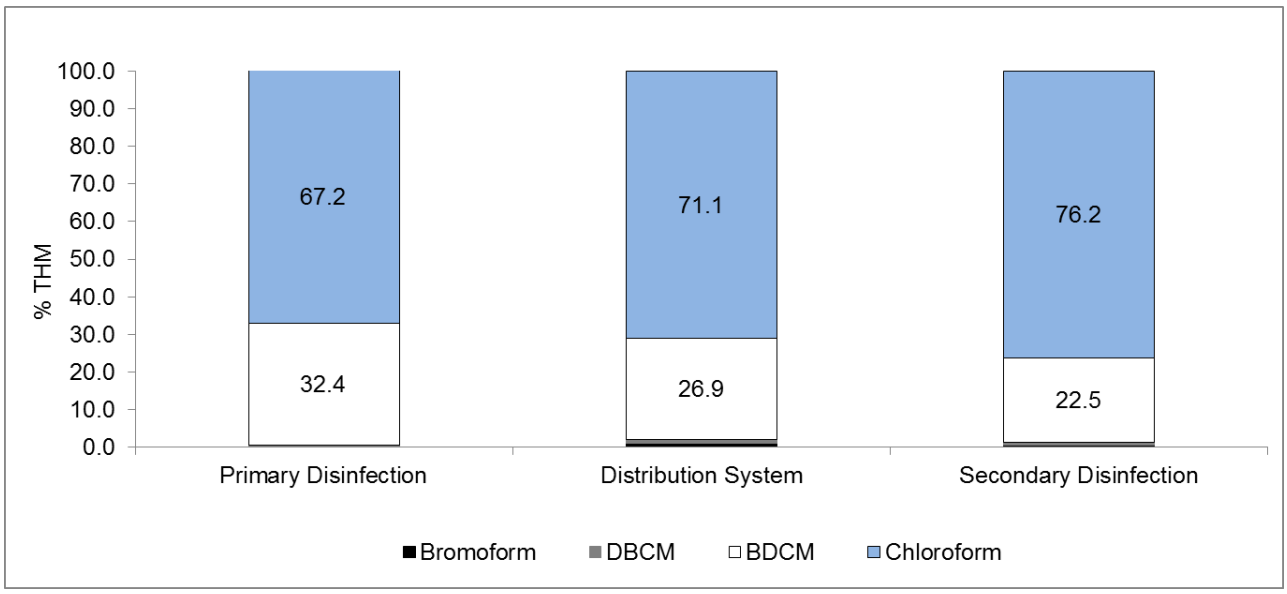


Figure 5-13: Average percentage distribution of the individual THM species within the WTP process flow system

The maxima and minima of each of the individual THM at each sampling point is indicated by the upper and lower lines within the box-and-whisker plots (**Figures 5-14** to **5-19**). When comparing the THM results after the various disinfection sampling points, it is obvious that the chloroform, BDCM and TTHM increases over time (**Figure 5-14**). Bromoform and DBCM measuring below the detection limit, did not show any variation within the distribution during the study period.

For all the four seasons, an increase was observed in the concentrations of TTHM, chloroform and BDCM within the distribution system when the contact time between NOM and chlorine was increased (**Figure 5-14**). According to Reckhow & Singer (2010), the highest THM concentrations during chlorination are expected at the greatest water age, due to increased contact time with chlorine even though the greatest THM formation occurs within the first 6 hours. It should also be noted that the increase in THMs after chloramination (secondary disinfection) is due to a larger residence time associated with chlorine and not the addition of monochloramine; this is because THM formation during chloramination is minimal (Howe *et al*., 2012; Chuang *et al*., 2013). Hourly differences in THM concentrations are also not as prominent in chloraminated systems, as THMs do not increase with water age compared to chlorination (Reckhow & Singer, 2010). From **Figures 5-14** to **5-17**, it is worth noting that the THM concentration in the chlorinated-chloraminated system increases in the order bromoform < DBCM < BDCM < chloroform. After chlorination, the average concentration of TTHM was 17.0 µg/L, 39.2 µg/L in the distribution system and 67.1 µg/L

after chloramination (**Figure 5-17**). These mean THM values in the final treated water are well below the regulated THM drinking water standard in South Africa (SANS 241:2015), confirming an effective organic matter removal by the WTP.

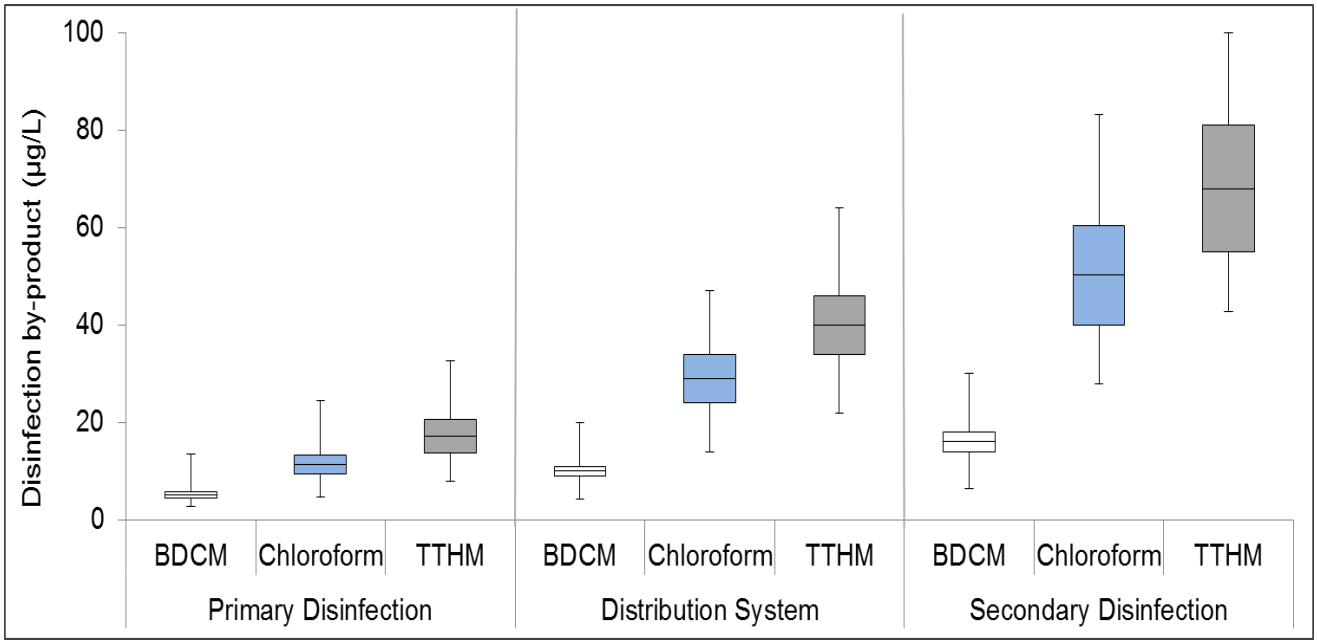


Figure 5-14: Spatial variability of THM formation within the WTP process flow system during the 12-month study period

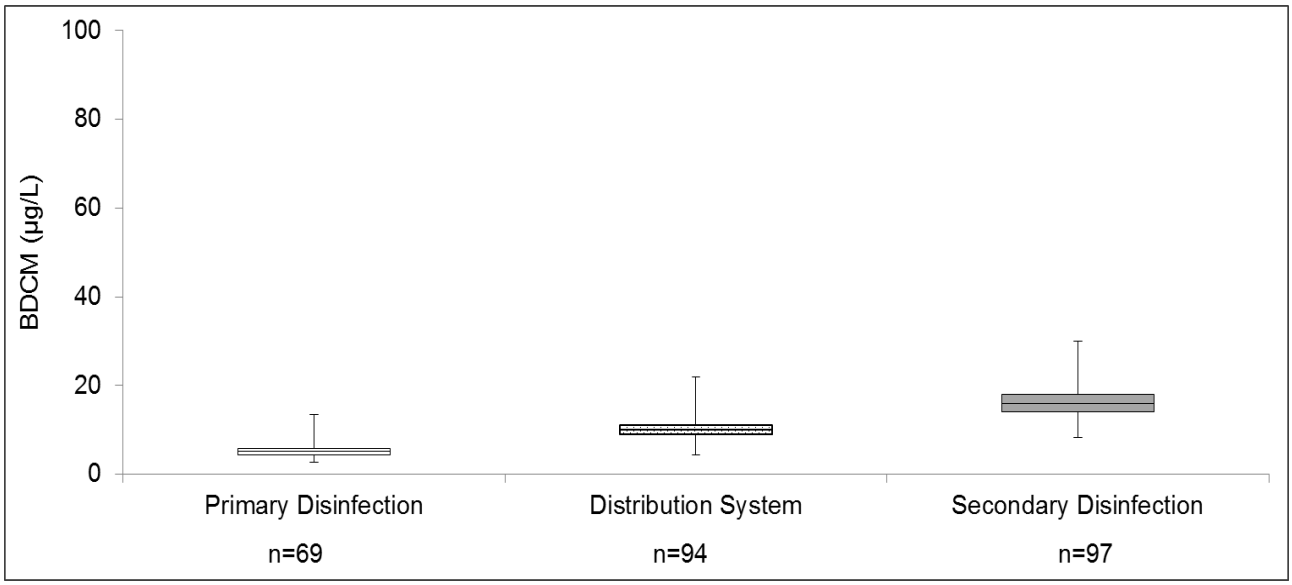


Figure 5-15: Variability of BDCM formation within the WTP process flow system during all four seasons

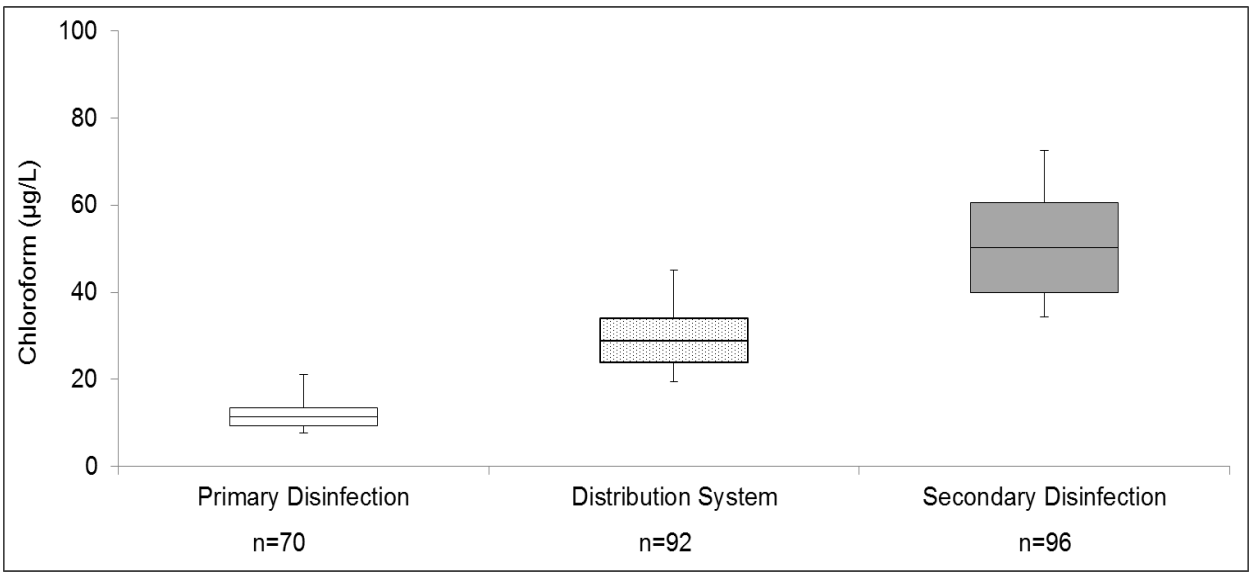


Figure 5-16: Variability of chloroform formation within the WTP process flow system during all four seasons

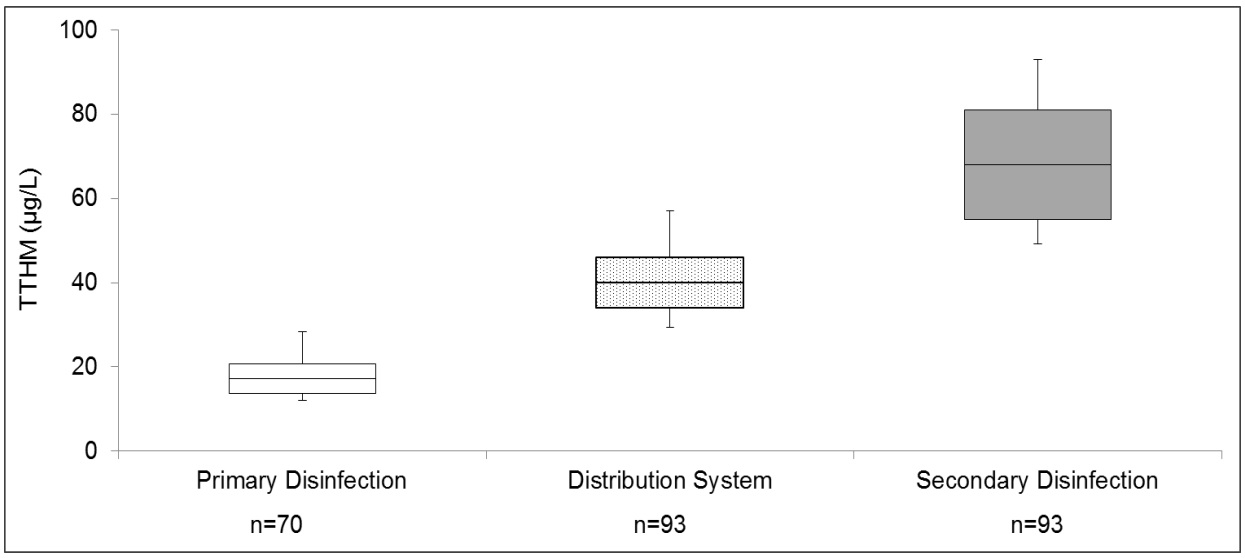


Figure 5-17: Variability of TTHM formation within the WTP process flow system during all four seasons

Figure 5-18 indicates the temperature of the water sampled in the distribution system during winter, spring and summer. At the primary disinfection plant chlorine dosage and chlorine demand showed diminutive variance during the study period (**Figure 5-19**). Chlorine dosage ranged between 3.0 and 4.3 mg/L with a mean value of 3.4 mg/L (**Figure 5-19**). As chlorine dosage was fairly constant at the full scale plant, it can be concluded that disinfectant dose did not have an effect on the THMs formed during the period of study (**Figure 5-14**). When taking into account the free chlorine residuals measured during disinfection, reduced

chlorine residuals were observed in samples from the distribution sampling point compared to water sampled at the primary disinfection process due to increased contact time (**Figure 5-20**). The depletion of chlorine led to an increase in THMs formed at the distribution sample point (**Figure 5-14**). Although chlorine dosage and NOM contact time does influence the yield of THM formation (Lu *et al*., 2009; Ramavandi *et al*., 2015), formation of THMs within the distribution system was primarily due to contact time of NOM fractions with chlorine as chlorine dosage displayed minimal variance during the study period (**Figure 5-19**).

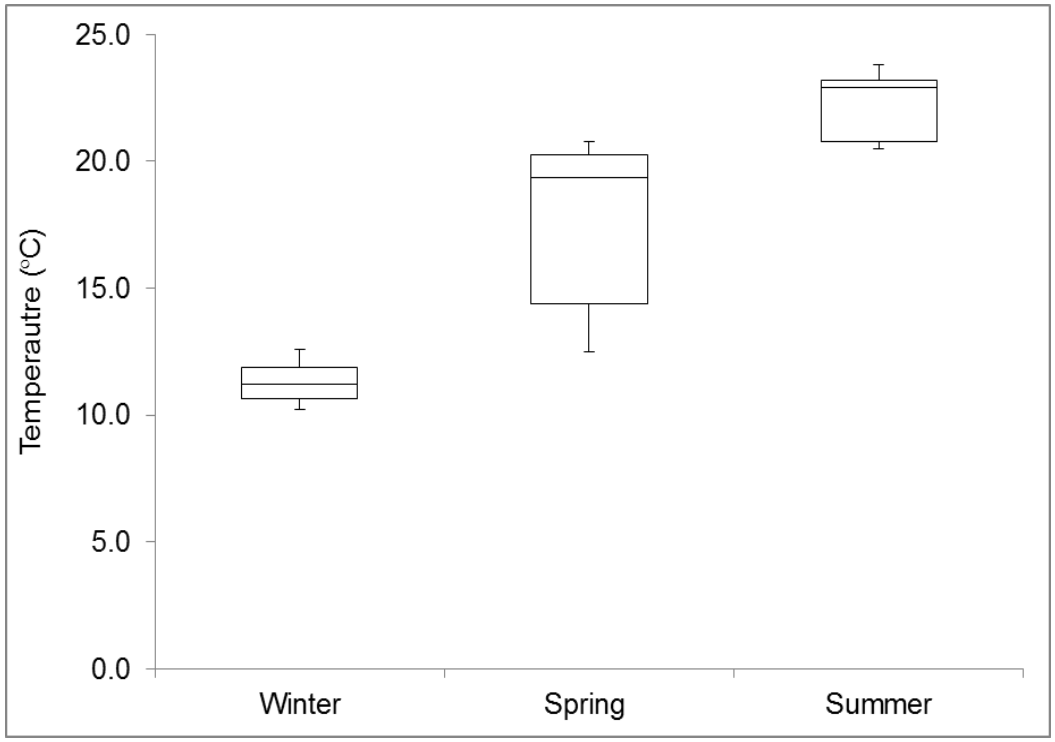


Figure 5-18: Seasonal temperature of water in the distribution system

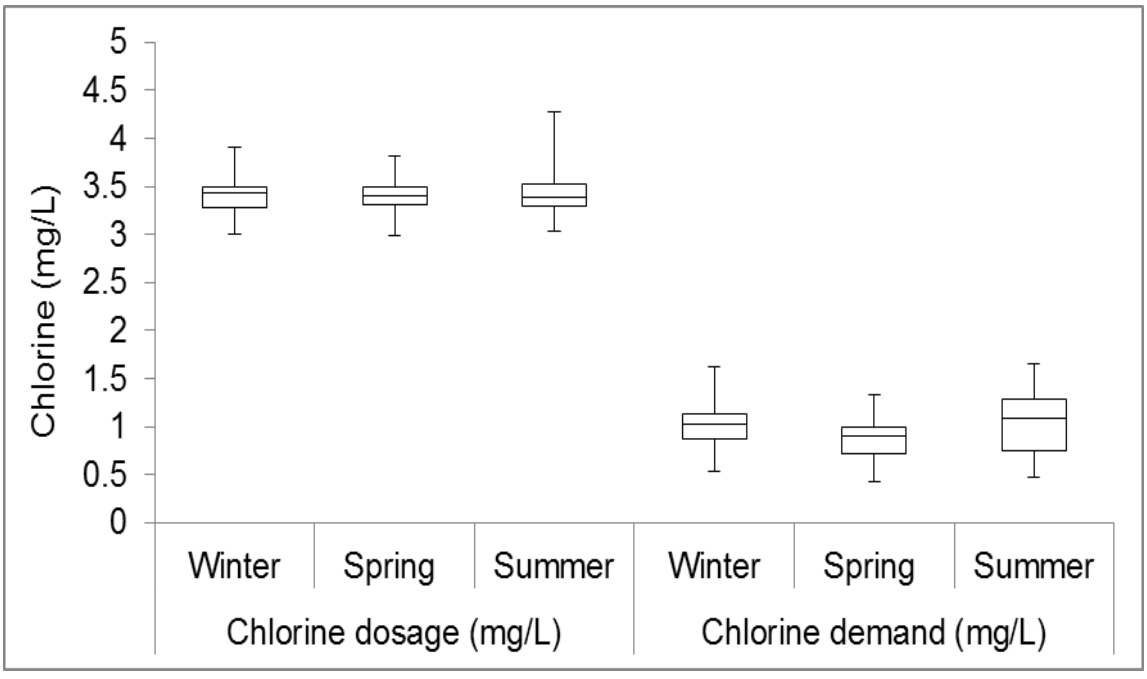


Figure 5-19: Chlorine dosage and chlorine demand at primary disinfection

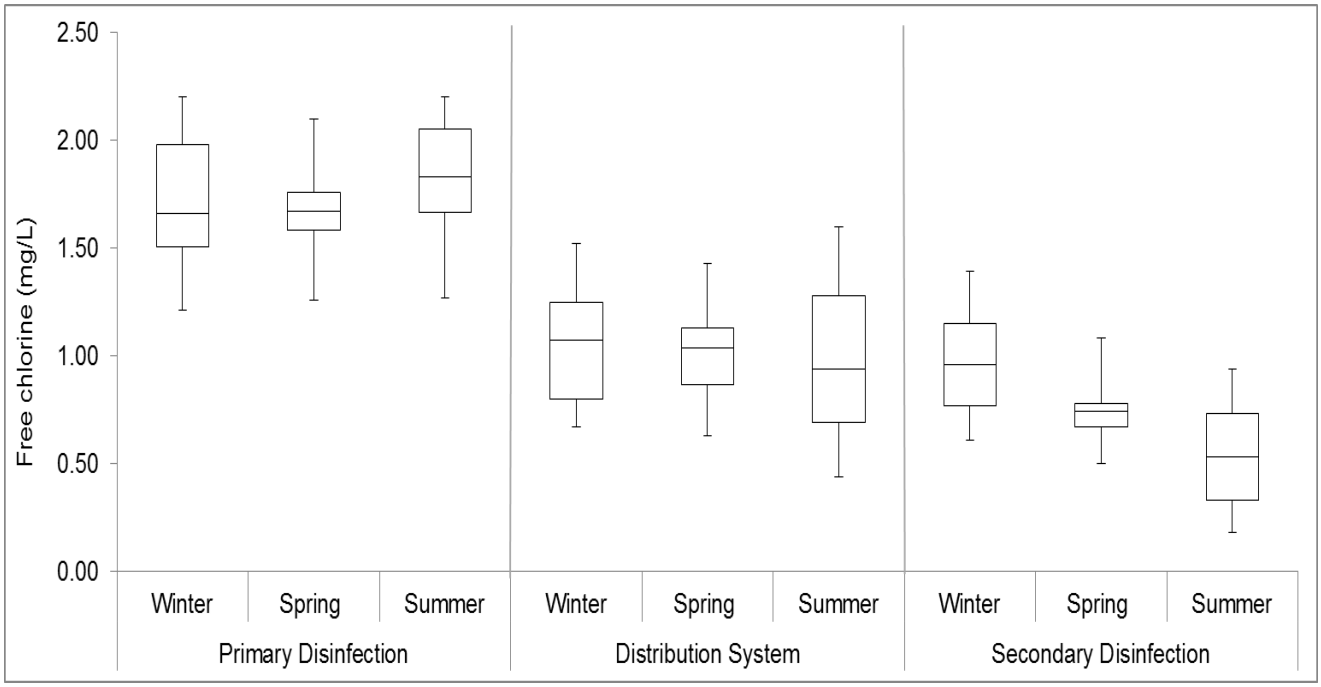


Figure 5-20: Free chlorine residual at the primary disinfection plant, at the sampling point between the chlorination and chloramination stages, and at the secondary disinfection plant

5.4 CONCLUSIONS

Due to limited data on NOM character within the Vaal Dam source water and seasonal variability of NOM highlighted in **Chapter 4**, this chapter assessed the effect of the structural NOM character on THM formation. Although it is well documented that NOM is the major initiator to the formation of THMs during chlorination and chloramination steps, the specific NOM fraction responsible for THMs during Vaal Dam surface water treatment had previously not been identified. In this chapter, the correlation between the molecular size distribution (MSD) of NOM and formation of the individual THM species was presented.

The main finding of the study presented in this chapter is that the HMW organic matter fraction was the primary precursor to the formation of chloroform, particularly during summer. Furthermore, by establishing the amount of aromatic NOM within the source water, typical NOM removal percentages by the full scale WTP can be predicted. This information should be valuable to WTP personnel as the SUVA value of the source water can be used

to predict the percentage removal of aromatic NOM that is likely to be achieved using the coagulation step of the WTP. The source water SUVA value can also provide useful insight to the treatability of HMW organic matter (having a high UV_{254} absorbing tendency), as water with higher SUVA values results in increased UV_{254} removal percentage of NOM. An analysis of the organic matter MSD revealed a noteworthy correlation between organic matter of larger molecular size (HMW) and THM formation, especially during the warmer summer months. This suggests that during summer chloroform formation is largely influenced by HMW NOM.

A weak correlation between source water SUVA and final water THM formation gave insight to the fact that the aromatic humic matter was not the only THM precursor during all the four seasons. Due to this weak correlation between SUVA and TTHM, the THMFP method (**Chapter 6**) will be utilised to predict the major NOM fraction (HPO, HPI or TPI) that is responsible for THM formation. The total concentration of the THM precursor material present within each of the NOM fractions responsible for the THM formation can therefore be determined using the THMFP technique.

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CHAPTER 6: THE USE OF FLUORESCENCE TO CHARACTERIZE FRACTIONATED THM PRECURSOR MATERIAL

6.1 INTRODUCTION

The purpose of this chapter is to demonstrate the significance of NOM characterization as well as the monitoring and removal of organic matter during plant operation to the potable water industry. This is motivated by the presence of inconsistent composition and character of organic matter in the Vaal Dam during various seasons and due to the divergent NOM character detected in different types of raw waters in South Africa (Nkambule, 2012). Various limitations exist that are associated with assessment techniques for variable NOM quantity and quality in South Africa. The specific objective of this chapter is therefore to assess advanced NOM characterization techniques that will provide an enriched understanding of the main fractions responsible for THM formation in final treated water. The outcomes emanating from this study will allow the South African WTP personnel within the bulk water surface industry to focus on a specific treatment technology targeted towards the efficient removal of these problematical fractions. This investigation will seek to identify a technique that can be effortlessly used within the global water industry to determine the major NOM fraction responsible for chlorine decay, which promotes THM formation during warm summer months.

6.2 EXPERIMENTAL DESIGN

The advanced fractionation and characterization techniques that are utilized during full scale water treatment and distribution include the modified polarity assessment method (m-PRAM), the enhanced biodegradable dissolved organic carbon (e-BDOC) and trihalomethane formation potential (THMFP) methods. The BDOC method will also be improved from a 6 day to a 4 day incubation period. Furthermore, Fluorescence Excitation Emission Matrix (FEEM) analysis will be performed on the m-PRAM and THMFP samples (during THM formation).

Figure 6-1 illustrates the sampling analysis flow diagram that was adopted for this study. The first step was to isolate and fractionate the organic matter into a HPO, HPI and TPI

fractions whereafter these fractIons were further characterized. The additional characterization steps and method development (enhanced-BDOC) for these fractions should:

i. Establish the treatability of the NOM fractions (sufficient removal by the WTP).
ii. Identify the problematic NOM fraction that requires attention during the drinking water treatment process.
iii. Produce a more rapid NOM characterization tool (enhanced-BDOC) for inclusion in a routine NOM characterization and monitoring protocol at drinking water treatment plants.

The problematic fraction is defined as a fraction that has high THMFP, is difficult to remove or is not successfully removed by the WTP, and is highly degradable by bacteria thus giving rise to biofilm formation within the distribution system.

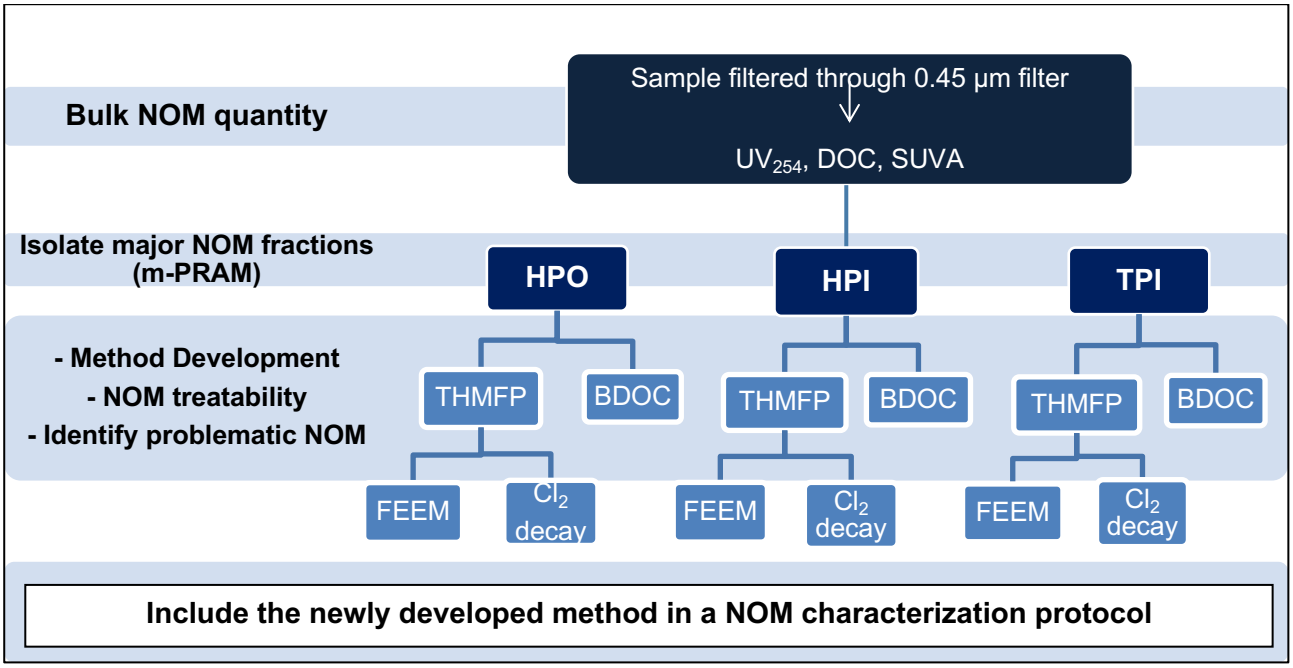


Figure 6-1: NOM fractionation and BDOC method development as part of the NOM characterization protocol

6.2.1 NOM fractionation by modified polarity rapid assessment method (m-PRAM)

The m-PRAM technique and optimisation experiments described in **Chapter 3** (**Sections 3.4.1** and **3.4.2**) were utilised for this investigation.

6.2.2 Method development for enhanced biodegradable dissolved organic carbon (enhanced-BDOC) analysis on NOM fractions

The 6 day BDOC method was used to determine the biodegradability of the fractionated NOM using the m-PRAM technique as described in **Chapter 3** (**Section 3.4**). This method has since proven to be a faster method for determining the bio-availability of the fractions and identifying the problematic NOM fraction. This technique was successfully improved leading to a decrease in the incubation time from 6 days to 4 days and ultimately resulting in an enhanced biodegradable dissolved organic carbon (enhanced-BDOC) measurement technique. The amended experimental conditions (nutrient salt addition, increased incubation temperature and decreased incubation time) were documented in **Chapter 3** (**Section 3.6.2**) and are discussed in **Section 6.3.4**.

6.2.3 Trihalomethane formation potential (THMFP) on m-PRAM fractions

The use of the THMFP technique was driven by the results obtained in **Chapter 5**, where a weak correlation between raw water SUVA and TTHM of the final treated water was observed. The THMFP analyses performed on the three major NOM fractions suggest the total concentration of THM precursor components present within each NOM fraction. The experimental conditions of the THMFP method are described in **Section 3.7** of **Chapter 3**.

6.2.4 Fluorescence excitation emission (FEEM) analyses during THMFP

FEEM analysis was performed on the NOM fractions after m-PRAM fractionation and also on samples obtained during the 7 day THMFP investigation. This was done to characterize further the change in NOM components following the chlorination step since the organic matter reacts with the chlorine. The method followed to obtain the FEEM data is described in **Chapter 3** (**Section 3.5**).

6.3 RESULTS AND DISCUSSION

6.3.1 Modified polarity rapid assessment method (m-PRAM)

The major modification in the m-PRAM has to do with the fact that it is a series technique that quantifies the amount of NOM possessing both HPO and HPI characteristics by filtering the same sample through all the three cartridges (C18→CN→NH_2). The filtrate of the C18 cartridge was filtered through the CN cartridge and eventually through the NH_2 cartridge to

obtain the TPI (charged) fraction. The eluent (0.1 M NaOH) eluted the HPO and HPI NOM from the C18 and CN cartridges, respectively.

The initial step conducted in m-PRAM was thorough cleaning of the SPE cartridges to remove possible UV_{254} absorbing contaminants located within the sorbent material of the cartridges. Thereafter, the UV_{254} breakthrough of the samples on each cleaned SPE sorbent was evaluated. The UV_{254} breakthrough curves obtained from the three cartridges using the m-PRAM technique are shown in **Figure 6-2**. The analyte samples displayed analogous breakthrough curves during the fractionation of HPO and HPI NOM using the C18 and CN cartridges. Whereas the initial breakthrough using from the C18 and CN cartridges occurred within 8 minutes, the breakthrough of the sample characterized by NH_2 was achieved after 6 minutes (**Figure 6-2**).

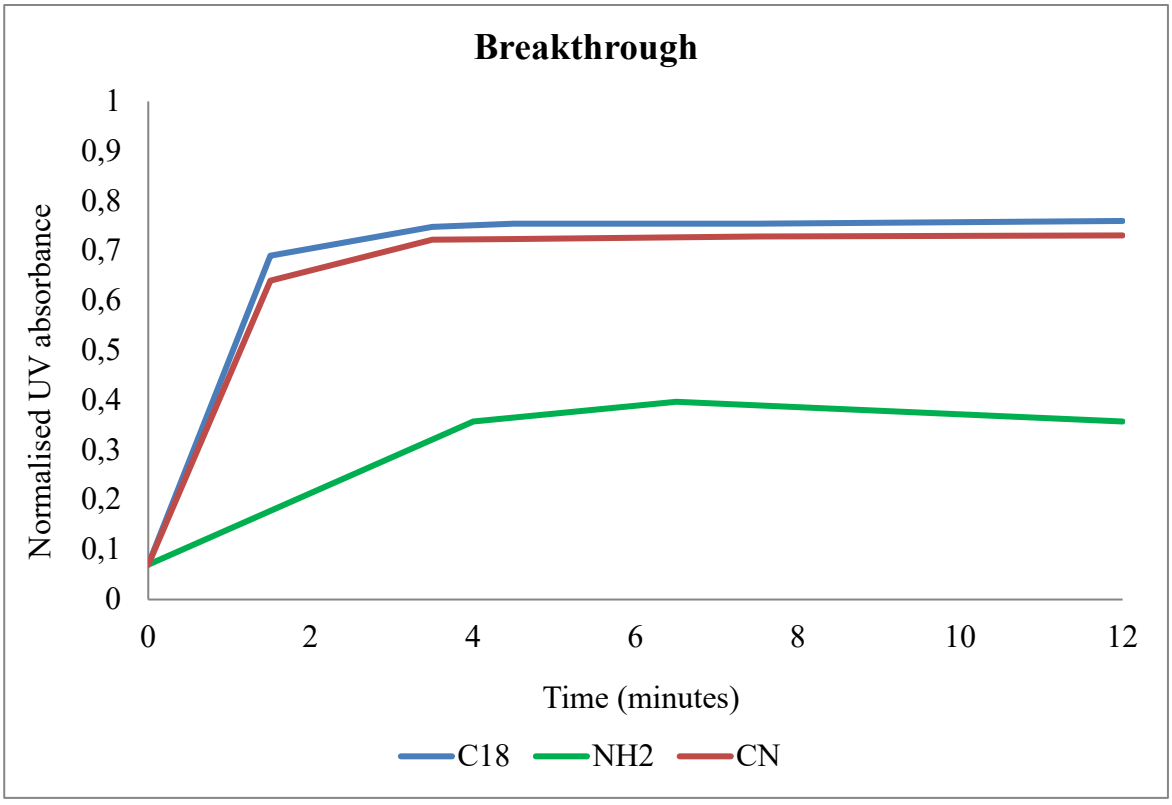


Figure 6-2: Typical breakthrough curve of the source water from the HPO (C18), HPI (CN) and NH_2 SPE cartridges presented as normalised UV_{254}

After collecting the filtered samples from the cartridges, the UV_{254} representing the aromaticity of each NOM fraction was measured after an initial breakthrough had occurred. The character of each NOM fraction was also quantified by presenting the UV_{254} value as a percentage. **Figure 6-3** shows a classical distribution of the HPI, HPO and TPI NOM fractions quantified during the study period using m-PRAM. It is evident that the HPO organic

matter fraction was removed during the full scale water treatment process. An increase in the HPI fraction eluted using the CN cartridges demonstrates the difficulties associated with the removal of the HPI NOM character by conventional water treatment techniques. A decrease in the charged fraction (TPI) was observed during the various full scale treatment steps. This is indicative of the efficiency of the WTP with regards to the neutralisation of charged organic matter during the treatment process (Philibert *et al*., 2008).

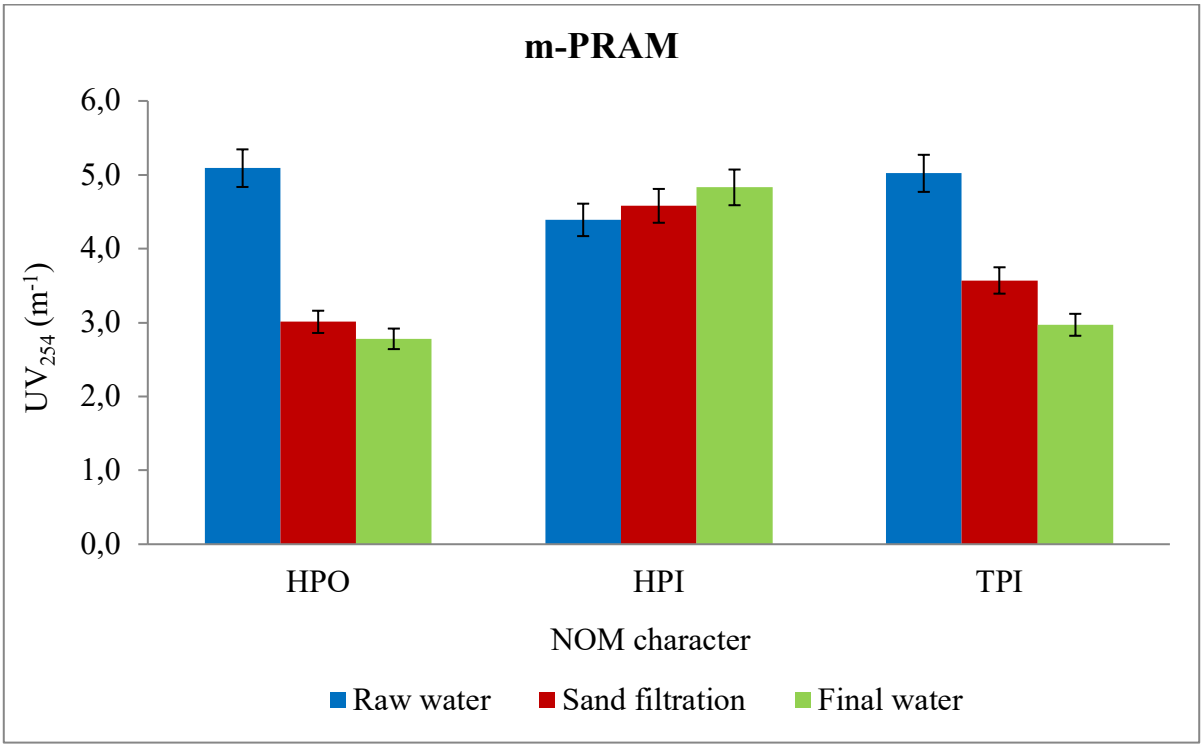


Figure 6-3: Classical distribution of UV absorbance at 254 nm of the HPO, HPI and TPI organic matter

Figure 6.4 illustrates the average percentage distribution of the HPO, HPI and TPI fraction within the source water (influent to the WTP) measured using m-PRAM UV_{254}. An almost equal distribution of the HPO, HPI and TPI NOM within the Vaal Dam source water is evident. This equal distribution of the source water having a HPO and HPI character concurs with the results outlined in **Chapter 4**, which show an average source water SUVA value of 4.5 L/mg.m during the period of June 2011 to February 2018.

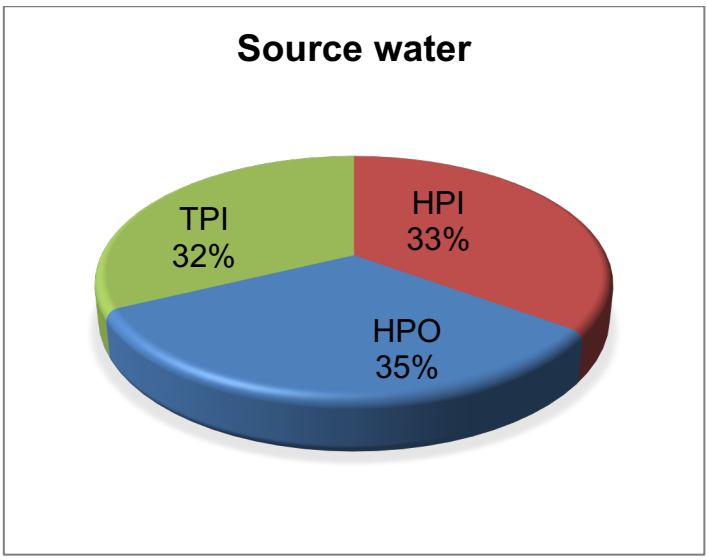


Figure 6-4: Average percentage distribution of the HPO, HPI and TPI fraction within the source measured by m-PRAM UV_{254}

A summary of m-PRAM results for the source water, water after full scale sand filtration and the final drinking water is presented **Figure 6-5**. A trend similar to the one shown in **Figure 6-3** was observed, whereby the HPO fraction is removed after treatment and the HPI NOM shows recalcitrance towards conventional water treatment processes. A similar distribution pattern of HPO, HPI and TPI NOM fractions within the source water is also shown in **Figure 6-5**. It can therefore be concluded that the HPI fraction in the sample increases during treatment and that both the HPO and TPI fraction decreases. The increase in post-conventional treatment of the HPI fraction observed in this study correlates with other findings (Chiang *et al*., 2002; Golea *et al*., 2017) where similar NOM fractionation and NOM treatability were assessed.

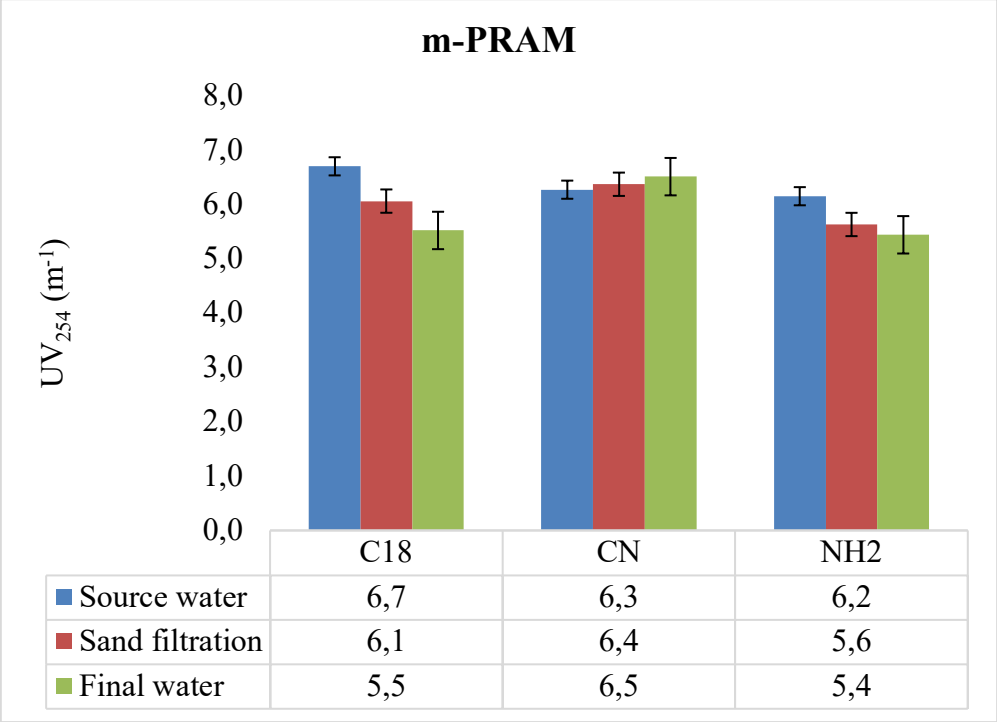


Figure 6-5: Average UV_{254} results from m-PRAM fractionation during full scale water treatment

6.3.2 Optimisation experiments of m-PRAM

In this section, another component was added to the washing step of the SPE cartridges during m-PRAM fractionation. The additional component entails the addition of 2 column volumes of methanol to the C18 and CN cartridges aimed at eluting from the SPE cartridges the organic carbon impurities, which are otherwise not eluted solely by washing with MQW (Chen *et al*., 2014). The MQW was then filtered through all three SPE cartridges until a steady-state UV_{254} was obtained. This occurred after flushing at least eight column volumes of MQW through the various cartridges for a period of 15 minutes. UV_{254} measurements were carried out on the methanol before and after filtering through the C18 and CN cartridges. **Figure 6-6** shows how the steady state UV_{254} absorbance was largely obtained after 12 minutes of filtering MQW through the various cartridges. To improve the cleaning step of the cartridges during m-PRAM, the cartridges were washed consecutively with 2 bed volumes (SPE cartridge) of methanol and MQW.

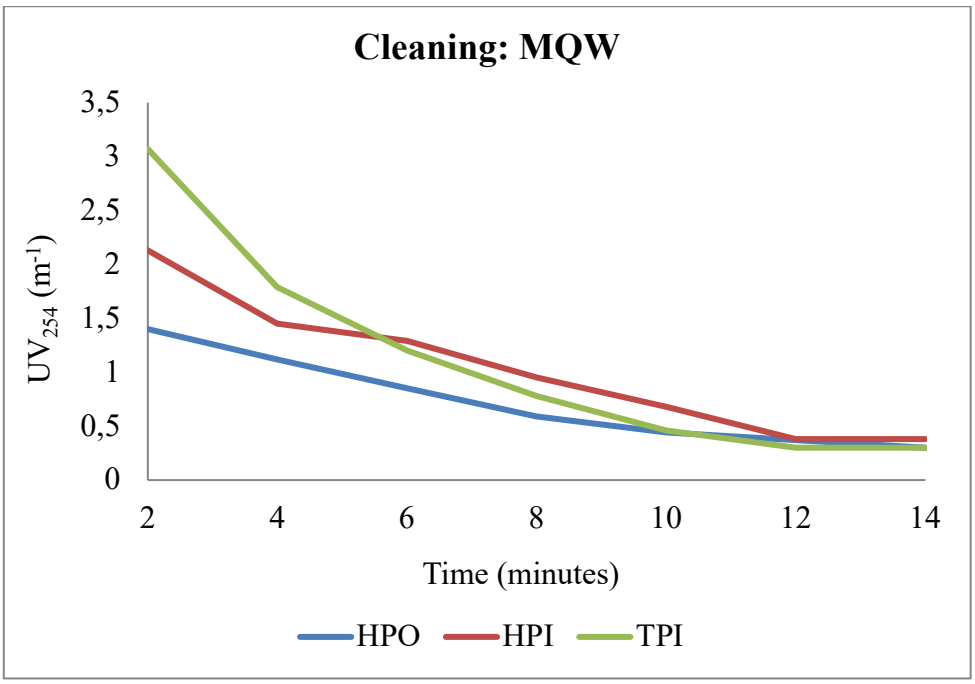


Figure 6-6: UV_{254} absorbance curves after cleaning the polar, non-polar and anion exchange SPE cartridges with MQW

Figure 6-7 shows how the steady state UV_{254} absorbance of the MQW was attained after 8 minutes of washing. According to the PRAM technique described by Rosario-Ortiz *et al*. (2004), a steady state UV_{254} can be obtained approximately 10 minutes following the flushing the cartridges with MQW.

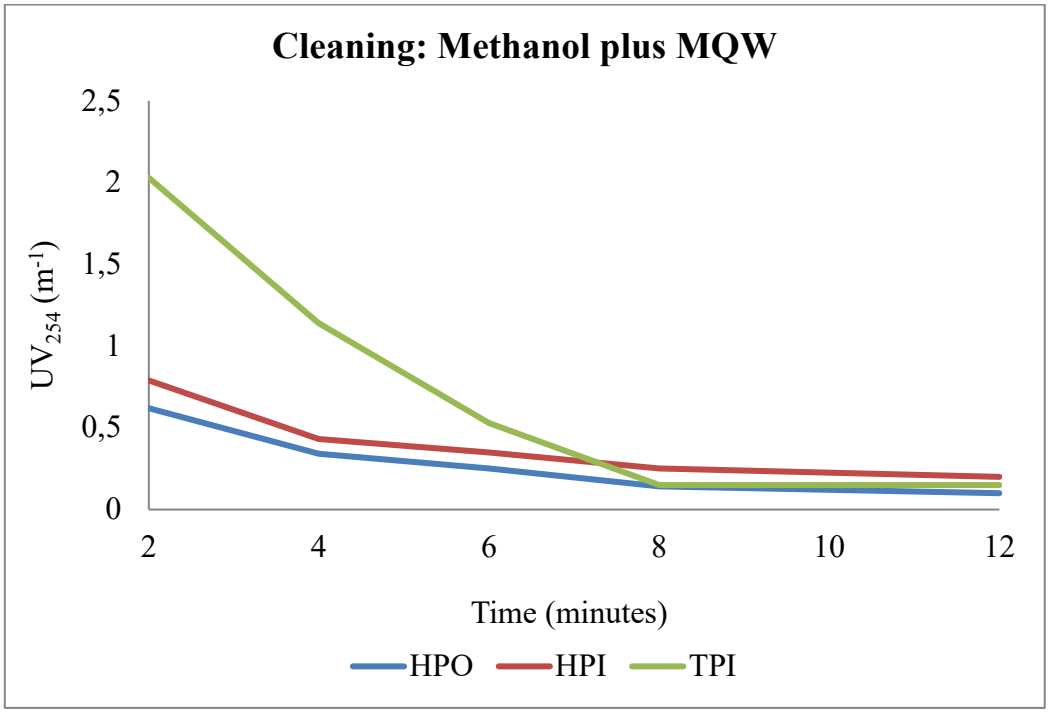


Figure 6-7: UV_{254} absorbance curves after cleaning the polar, non-polar and anion exchange SPE cartridges with methanol and MQW

The second m-PRAM analysis step involved obtaining the breakthrough curve from each SPE sorbent on the sample analysed. The sample was first filtered through a membrane filter (0.45 µm) followed by filtering through the three cartridges at a flow rate of 1.2 mL/min (5 inches Hg, 0.1 bar). A comparative analysis of the breakthrough curves obtained during the two cleaning steps (MQW vs methanol followed by MQW) is illustrated in **Figure 6-8**. When using m-PRAM for extraction of the HPO, HPI and TPI NOM identical breakthrough curves were obtained from the source water after cleaning the cartridges using MQW, compared to when using methanol followed by MQW. Therefore, although the added methanol step during PRAM fractionation improved the cleaning step by achieving a steady state UV_{254} reading of the MQW faster (**Figure 6-7**), the time for the breakthrough in the sample is similar, meaning limited influence as compared to cleaning without methanol.

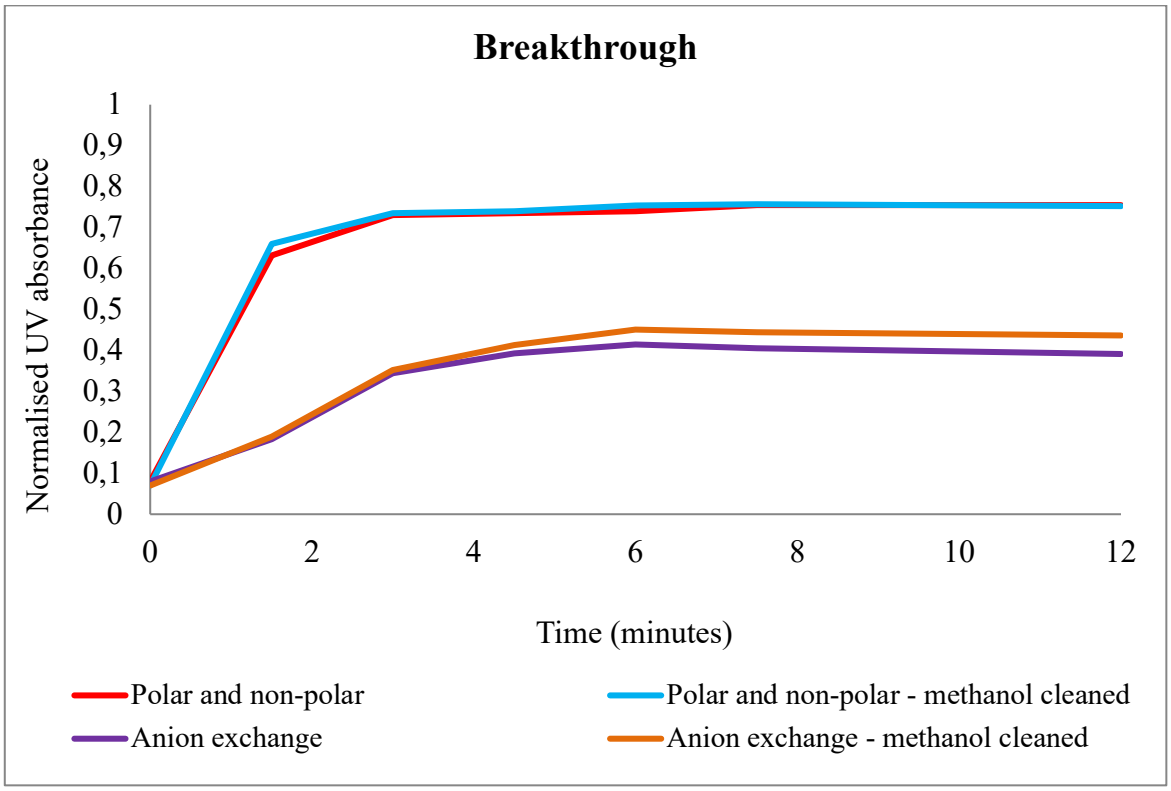


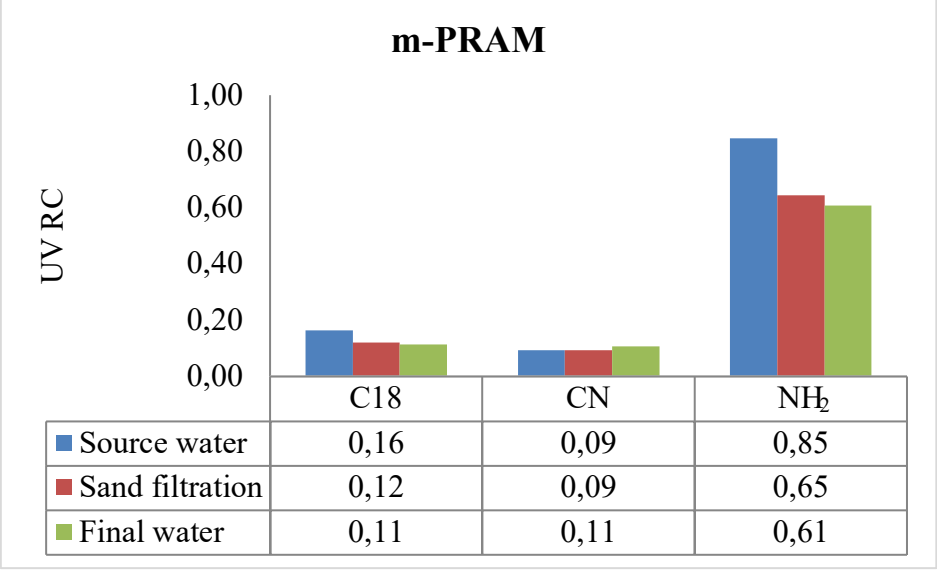
Figure 6-8: Breakthrough curves (normalised UV_{254}) of the source water following cleaning of the cartridges with MQW and methanol and MQW

The m-PRAM experiments were performed in duplicate and were run on the source water samples, water samples obtained from full scale sand filtration and on the final treated water samples. The results of these experiments were presented as retention coefficient (RC) of each SPE sorbent. The RC portrays the fraction of UV_{254} absorbing material within the samples that was adsorbed onto the various cartridges after initial breakthrough had occurred. The RC values were calculated as shown in **Equation 3.2**.

$$RC = 1 - \frac{C_{max}}{C_0} \quad [3.2]$$

where RC is the retention coefficient, C_{max} is the maximum breakthrough obtained during the extraction and C_0 refers to the UV_{254} value of the original sample before fractionation (Rosario-Ortiz *et al*. (2007).

Figure 6-9, which summarises the RC values of each of the cartridges illustrates that similar proportions of HPO and HPI NOM are present in the water samples. A decreasing trend in the RC value of the C18, C8 and C2 cartridges indicate that the conventional WTP removes some of the HPO organic matter. As illustrated by an increase in the RC values obtained using the CN cartridge, removal of the HPI component of NOM was not achieved in the source water compared with the final treated water. The RC results shown in **Figure 6-9** agree with the work carried out by Philibert *et al*. (2008), where HPO NOM was removed while the HPI component during water treatment typically increased. A decrease in the RC values associated with NH_2 SPE confirms the removal of the charged fraction of NOM during water treatment. According to Philibert *et al*. (2008), the NH_2 RC values obtained during the water treatment steps essentially prove the effectiveness of the performance of a plant with regards to the neutralisation of the charged NOM fraction (coagulation). As shown in **Figure 6-9**, a decrease in the HPO and TPI fractions can be clearly seen, with the HPI NOM fraction not being removed at all during the water treatment process.



	C18	CN	NH_2
Source water	0,16	0,09	0,85
Sand filtration	0,12	0,09	0,65
Final water	0,11	0,11	0,61

Figure 6-9: Change in polarity of NOM during full scale water treatment as indicated by RC values from m-PRAM (n=22)

It can be concluded from the RC results shown in **Figures 6-9** and **6-10** that organic matter is capable of having functionalities in both HPO and HPI regions when m-PRAM technique is applied. This was demonstrated by the achievement of a total RC value that is not always

exactly equal to 1. Furthermore, the main advantage of PRAM is that the sequence in which a sample is filtered through the various polar and non-polar cartridges can be either parallel or series (Philibert *et al*. 2008). Fractionation by m-PRAM highlights the general hydrophobicity (C18), hydrophilicity (CN) and charge neutralisation (NH_2) of NOM during the full scale water treatment process.

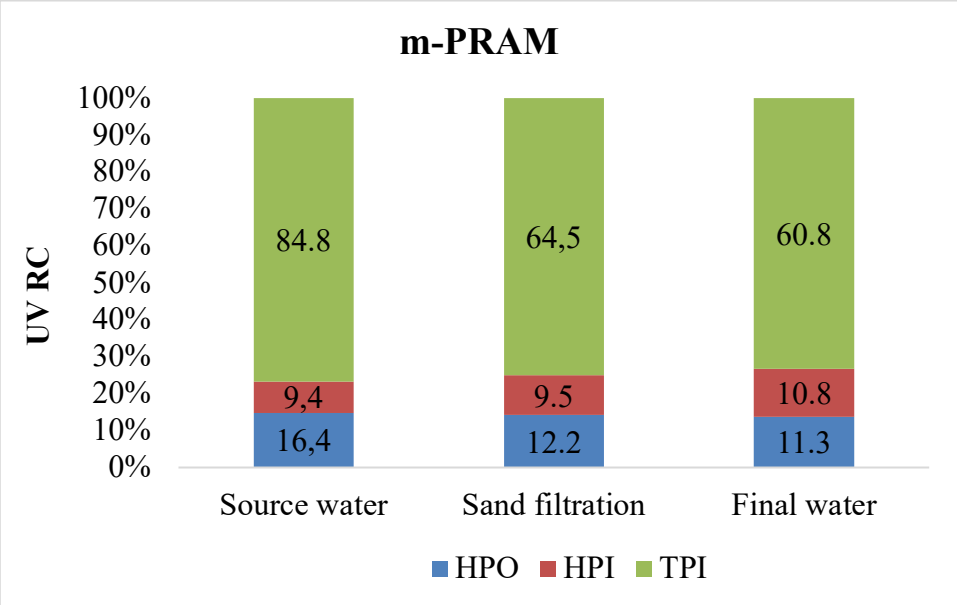


Figure 6-10: Percentage RC values of the HPO, HPI and TPI NOM fractions during full scale water treatment

Following fractionation using modified-PRAM the various fractions after initial UV_{254} breakthrough were analysed for DOC. The DOC data was utilised for the calculation of mass balance (**Table 6-1**) for determining possible carbon leaching from the sorbents as well as the % recovery from the cartridge. Since the m-PRAM technique was combined with other characterization techniques, it is crucial that the NOM divided into the various fractions be a true representation of the isolated fractions. The DOC values of the individual fractions were also used during the mass balance calculation to determine possible leaching from the cartridges and evaluate the percentage recovery of organic carbon by each SPE cartridge. An initial sample volume of 2 L was filtered through 0.45 µm filter paper and analysed for DOC (referred to as Bulk water in **Table 6-1**). The volume of sample filtered through the C18 and CN cartridges during m-PRAM fractionation was 300 mL, and 500 mL through the NH_2 cartridge; 300 mL of this volume was utilised for the BDOC (**Section 6.3.3**) and THMFP (**Section 6.3.5**) experiments. **Table 6-1** provides an example of the DOC results obtained of the various fractions after m-PRAM and were used for a mass balance calculation, with Samples A and B being duplicate analysis. From **Table 6-1**, 93.8 to 95.7% of the organic

carbon was recovered after m-PRAM fractionation indicating satisfactory fractionation using the modified-PRAM technique.

Table 6-1: DOC fractionation results obtained from m-PRAM

Fraction	DOC (mg/L)		Sample vol. (L)		DOC mass (mg)	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
Source water						
Bulk water	4.9	4.6	2.0	2.0	9.8	9.2
HPO	7.5	6.2	0.3	0.3	2.3	1.9
HPI	5.0	4.8	0.3	0.3	1.5	1.4
TPI	11.0	11.0	0.5	0.5	5.5	5.5
Total DOC mass (HPO + HPI +TPI)					9.3	8.8
DOC Recovered (%)					**94.4**	**95.7**
Treated water						
Bulk water	4.5	4.2	2.0	2.0	9.0	8.4
HPO	8.8	6.0	0.3	0.3	2.6	1.8
HPI	4.5	3.9	0.3	0.3	1.4	1.2
TPI	8.9	10.0	0.5	0.5	4.5	5.0
Total DOC mass (HPO + HPI +TPI)					8.4	8.0
DOC Recovered (%)					**93.8**	**94.9**

6.3.3 Biodegradable dissolved organic carbon (BDOC) on NOM fractions

The biodegradable NOM fraction was quantified using the standard 6-day BDOC experiment by measuring the initial DOC and the refractory dissolved organic carbon (RDOC) at the end of the incubation period. The RDOC is also known as the non-biodegradable dissolved organic carbon (NBDOC) fraction, illustrating the DOC that is not biodegraded by the bacteria and is obtained when the DOC value reaches a plateau (**Figure 6-11**). The decrease in DOC is due to heterotrophic bacteria attached on the sand that oxidises the biological available carbon within the various samples. A typical biodegradation curve representing the mineralisation of DOC by the bacteria is illustrated in **Figure 6-11**. The biodegradation of each NOM fraction was calculated from the difference between the initial DOC and NBDOC, thereafter expressed as percentage BDOC since the DOC within the source water fluctuates.

The NBDOC value in **Figure 6-11** represents the minimum DOC (DOC_{min}) achieved. The BDOC was calculated using the following equation:

$$BDOC = DOC_{initial} - DOC_{min} \quad [6.1]$$

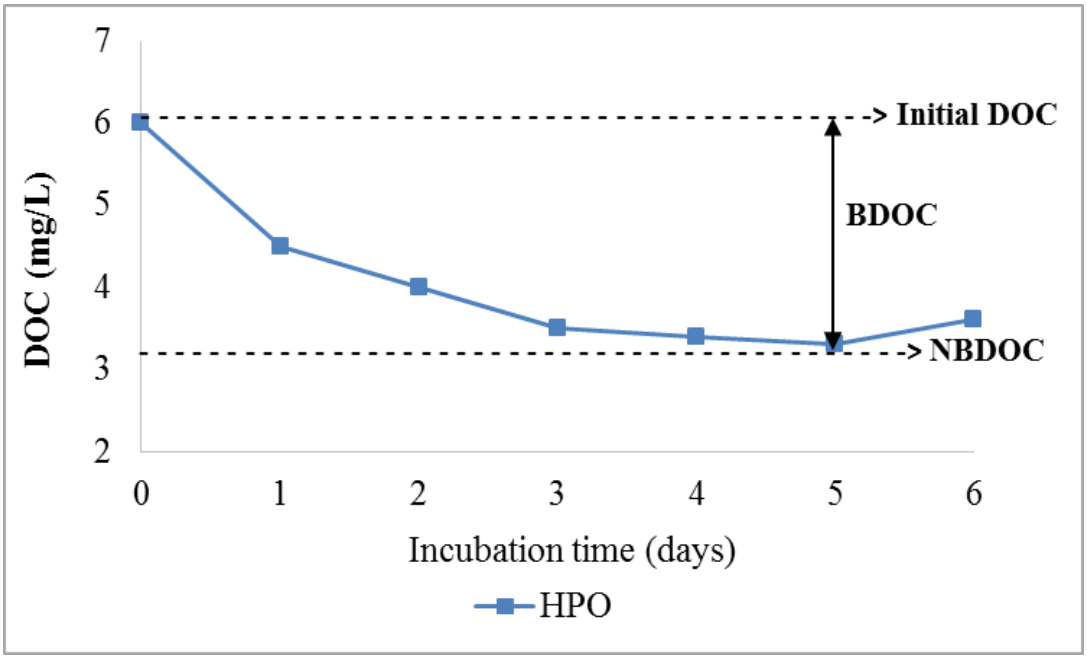


Figure 6-11: Typical biodegradation curve of the HPO NOM fraction

Figure 6-12 and **Table 6-2** shows a typical decrease of DOC in the HPO, HPI and TPI NOM fractions obtained during the standard 6 day incubation period. The control used to establish whether the bacteria cultivating the sand were biologically active was sodium acetate ranging in concentration of 5-10 mg/L. Such a sodium acetate concentration range was adopted since the DOC of the source water falls within this DOC range. Sodium acetate is often used during biodegradation studies and is easily biodegraded by bacteria (Escobar & Randall, 2001; Park *et al*., 2004; Yapsakli & Çeçen, 2009). According to organic matter biodegradation studies, approximately 88% of the organic carbon in the control samples was metabolised within 6 days (McDowell *et al*., 2006). When a concentration of 1-8 mg/L sodium acetate was used, most of the acetate was mineralised within the first day of incubation (Menge *et al*., 2009). This corresponds to the high percentage of DOC degraded within the sodium acetate observed in the BDOC experiments within this study, indicating the presence of active bacterial cultures on the sand (**Figure 6-12**).

According to Joret *et al*. (1991), 10-30% of the DOC found in drinking water is biodegradable. An analysis of the 6-day BDOC method revealed that the average % BDOC obtained in the source water was 33.6%. On the other hand, the respective BDOC levels of 36.8%, 31.8% and 32.1% were recorded for HPO, HPI TPI NOM fractions (**Figure 6-13**). It should be noted that the minimum DOC was only reached on the fifth day of the 6-day BDOC analysis period (**Figure 6-12** and **Table 6-2**). As reported in the study undertaken by Nkambule (2012), bulk

(unfractioned) Vaal Dam source water was found to possess BDOC levels ranging between 46.0 and 48.0%. A study that investigated drinking water from a Namibian reclamation plant and a conventional WTP documented BDOC levels of 30% and 20%, respectively (Menge *et al*., 2009).

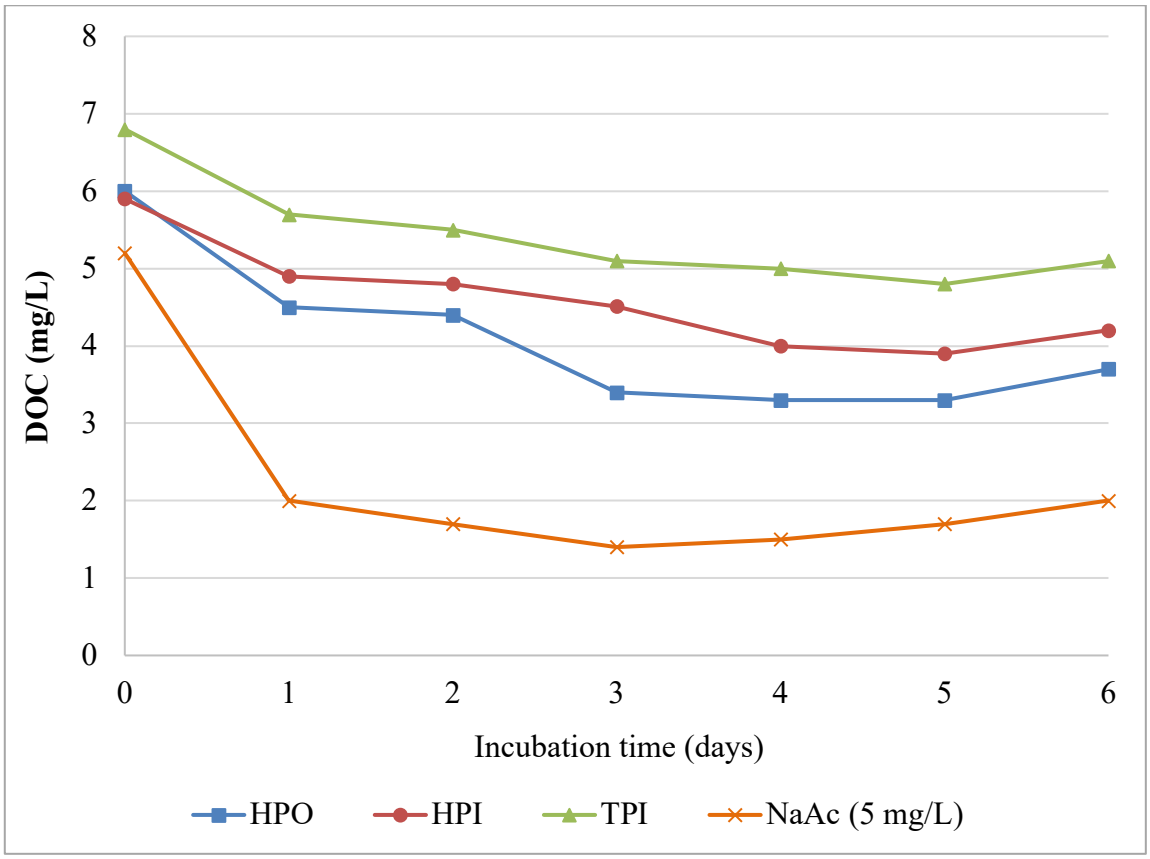


Figure 6-12: Biodegradation curve for DOC fractions and NaAc (sodium acetate) over 6 days

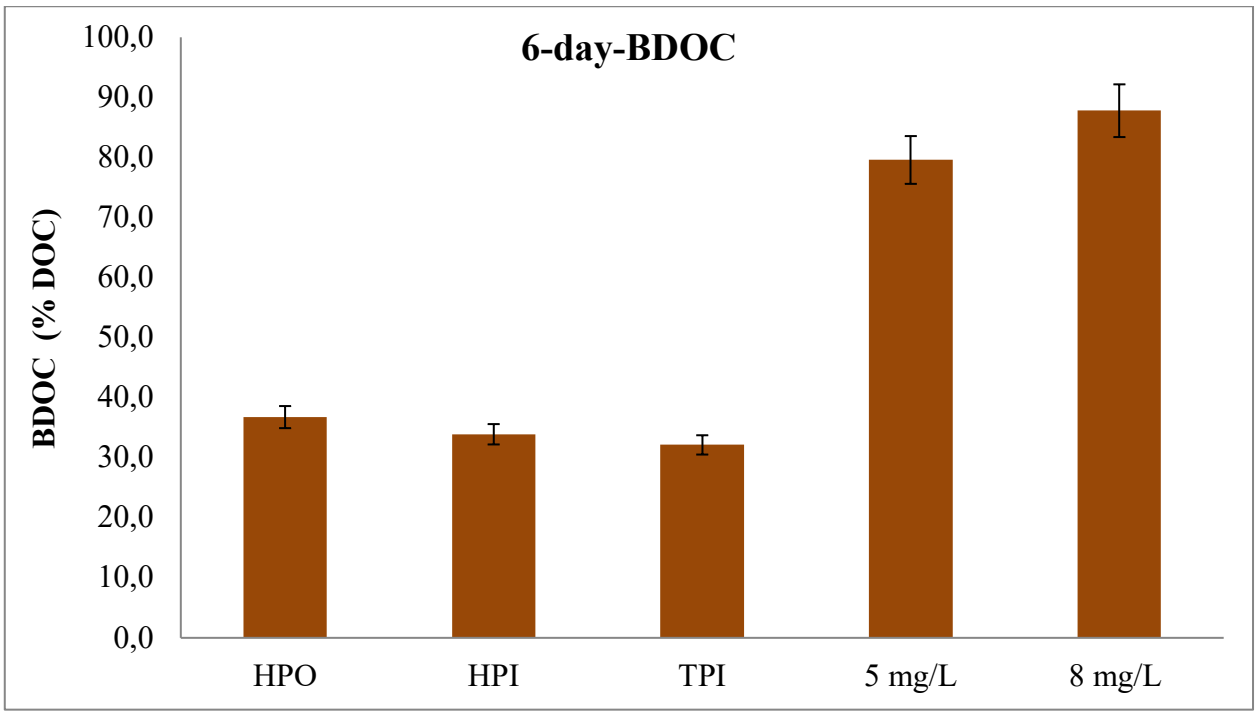


Figure 6-13: Average percentages BDOC of the individual NOM fractions and NaAc (sodium acetate) control samples obtained from the original BDOC method

Table 6-2: Typical decrease in DOC values during the standard 6-Day BDOC experiment

Standard 6-day BDOC									
Fraction	d0	d1	d2	d3	d4	**d5**	d6	BDOC	NBDOC
HPO	6.4	6.1	6.0	6.0	5.5	**3.7**	5.1	2.7	3.7
HPI	5.9	4.9	4.8	4.5	4.0	**3.9**	4.4	2.0	3.9
TPI	6.0	5.6	5.5	5.1	5.0	**4.8**	5.2	1.2	4.8

6.3.4 Enhanced biodegradable dissolved organic carbon (enhanced-BDOC) on NOM fractions

The ultimate aim of the BDOC analysis of this study was not to simulate the growth conditions of drinking water bacteria found within the distribution system but to determine the DOC fraction that is more readily oxidised by drinking water bacteria, which is depicted by highest biodegradability of the organic matter fraction. It is this type of NOM fraction that is associated with bacterial growth and needs to be removed during the water treatment process in order to limit biofilm formation within the distribution system.

The preference of carbon utilisation by bacteria relies greatly on the type of inoculum (bacteria) used since bacterial cultures adapt to the substrate within its environment (Mishra & Srivastava, 1998; Trulleyova & Rulik, 2004). In this study, a well-adapted heterogeneous bacterial culture, which was sourced from the sand of a full-scale rapid gravity sand filter,

was sampled before the pre-scheduled backwash cycle of the sand filter (backwash occurs every 48 hours). A heterogeneous bacterial culture has a higher biodegradation capacity than a single strain of bacteria used for the BDOC estimation (Servais *et al*., 1989).

Furthermore, to augment the 6 day BDOC analytical method, the temperature was increased from 20 ˚C (as per original method of Joret *et al*., 1989) to 30 ˚C. Various water-based bacteria including gram-negative aerobic *Pseudomonas,* optimally grow at temperatures ranging between 25 ˚C and 30 ˚C (Allen *et al*., 2004; Sharp, 2004; Bitton, 2014). When a BDOC assay investigation was undertaken by Kaplan *et al*. (2004), a sodium acetate BDOC value of 77% was achieved when a sand-biofilm reactor column operated at 15 ˚C was employed. This contrast sharply with the 89% BDOC levels that were achieved when bacteria attached to sand method was incubated at 20 ˚C (Joret *et al*., 1989). It is therefore possible that temperature has an effect on the biodegradation process.

According to a study by Schmidt & Alexander (1985), heterogeneous bacterial culture and single strains of bacteria are able to simultaneously degrade aromatic carbon and other organic compounds through the addition of acetate or glucose. Simultaneous substrate uptake by bacteria is however concentration dependent. Whereas acetate was completely mineralised before phenol degradation (acetate addition of 70 µg/L), simultaneous mineralisation of phenol and acetate occurred at concentrations of 2 µg/L and 13 µg/L, respectively (Schmidt & Alexander, 1985). The study by Schmidt & Alexander (1985) was performed over a period of 7 days and temperature of 21 ˚C in an inorganic nutrient salt solution containing NH_4Cl and KH_2PO_4 (including Na_2HPO_4, NH_4Cl, $MgSO_4$, CaCl, FeCl, $MnSO_4$, $ZnSO_4$, $CuSO_4$ and CoCl).

From the study of Mishra & Srivastava (1998) the growth of *Pseudomonas* cultures were investigated in a salt medium containing phosphate and ammonia by studying the oxidation of aromatic substances when using two carbon sources (phenol and glucose). Results from this study indicated that bacterial cultures adapt to the carbon source available and the specific growth rate of bacteria is higher when different carbon sources are available (Mishra & Srivastava, 1998). Therefore, not only is the consumption of a carbon source by bacteria dependent on the type of bacterial inoculum used, it also depends on the adaptation of the bacterial culture towards the carbon source. According to Labanowski & Feuillade (2009), the abundance of compounds that are easily biodegraded could enhance the bacterial degradability of NOM in surface waters.

In biodegradation assessments nutrient limitation is possible and often accompanied by an increase in the DOC results during the incubation period, due to lysis of the bacterial cells (Volk *et al*., 1994; Menge *et al*., 2009). Within this study an increase in DOC after day 5 (**Figure 6-12** and **Table 6-2**) is also evident. In the study by Menge *et al*. (2009) a minimum DOC was reached on day 3 (d3) whereafter an increase of DOC was observed from d3 until day 5 (d5) during their investigation of fast and slow biodegradable organic carbon compounds. Increases in DOC after the minimum DOC value was achieved, was also documented by Kaplan *et al*. (2004).

Schmidt & Alexander (1985) have reported that the addition of a second substrate is capable of increasing the biodegradation rate of organic compounds. In an experiment undertaken by Labanowski & Feuillade (2009), a nutrient solution containing 20 mg/L C was added to nutritive growth solution during BDOC quantification in order to support bacterial growth. This nutritive solution is similar to that utilised by Reuschenbach *et al*. (2003) during normalised biodegradation tests, which was primarily focussed on DOC die-away tests (OECD 301 and ISO 14593). Other bacterial decomposition (in soil/phenol/glucose) studies have incorporated the addition of inorganic nutrients or autochthonous/ allochthonous organic carbon for the degradation of phenol or glucose (Kalbitz *et al*., 2003; McDowell *et al*., 2006; Attermeyer *et al*., 2014). An investigation to enhance bacterial degradation (by addition of autochtohonous and allochthonous carbon) resulted in an increase of up 68% DOC consumption without limiting nitrate and phosphate nutrients (Attermeyer *et al*., 2014).

For the enhanced BDOC assessment undertaken in this project, inorganic salt nutrients were added to each sample at the start of the incubation period to limit nutrient deficiency. The average N and P concentration in the source water was 0.04 mg/L and 0.12 mg/L, respectively. Potassium dihydrogen phosphate (KH_2PO_4, 0.1%) and ammonium chloride (NH_4Cl, 0.1%) were prepared followed by the addition of 50 mL of each nutrient solution to the biological activated sand (BAS) containing the HPO, HPI and TPI fractions. Each 500 mL Schott bottle contained 300 mL sample, 50 mL nutrient salt solution and sand (~100 g). Microbial activity of bacteria attached to the sand was evaluated during each BDOC experiment using sodium acetate as control.

Table 6-3 presents the typical decrease in DOC observed during the 4 day BDOC analysis where the incubation time was decreased from 6 days to 4 days, to be a less time consuming NOM characterization tool. For the novel enhanced 4-day BDOC method, minimum DOC values were observed on day 3 of the incubation period (**Table 6-3**).

The average % BDOC obtained in the source water was 35.0% for the 4-day BDOC study. Furthermore, BDOC levels of 41.9%, 34.3% and 35.3% were observed for the respective biodegradation of HPO, HPI and TPI NOM fractions under the same conditions (**Figure 6-14**).

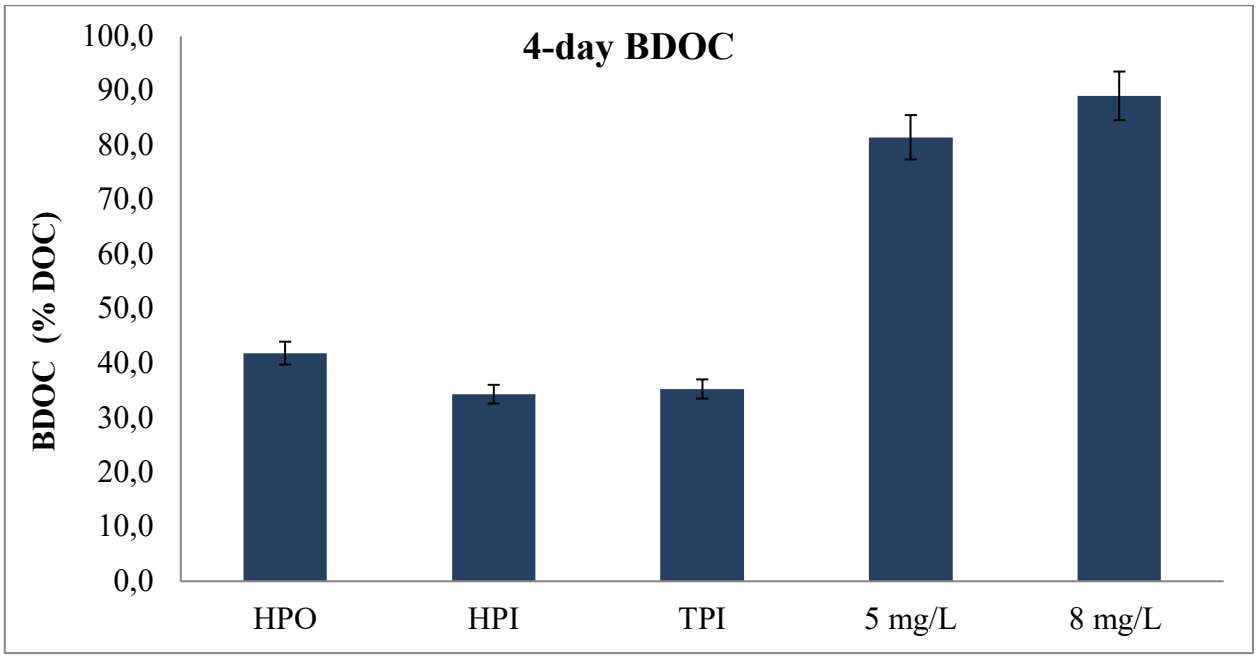


Figure 6-14: Average percentages BDOC of the individual NOM fractions and NaAc (sodium acetate) control samples obtained from the enhanced-BDOC method

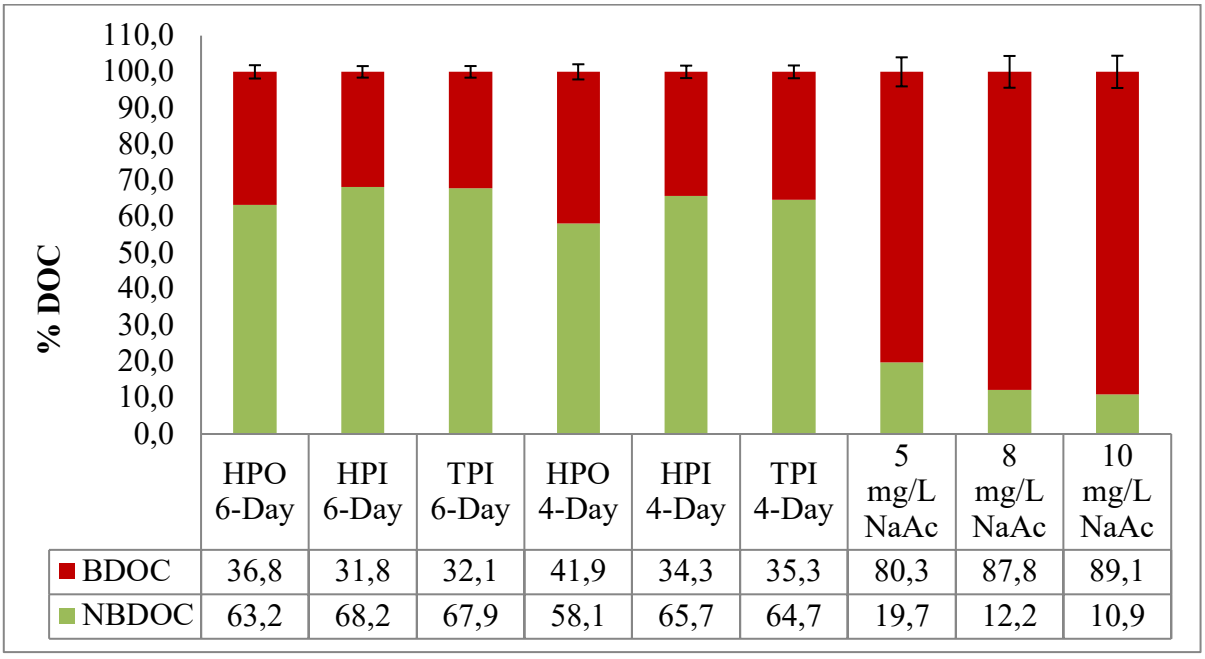
With reference to the enhanced 4-day method, biodegradability of the NOM in the source water was largely attributed to the HPO fraction. Therefore, although these results indicate that all three fractions are mineralised by the bacteria, the HPO fraction is much more susceptible to bacterial degradation. The high degradation rate associated with the HPO fraction in the surface water sample was corroborated by Labanowski & Feuillade (2009) who found that the HPO fraction tended to be more reactive towards microorganisms. Labanowski & Feuillade (2009) recorded BDOC levels of 12% for the biodegradation of the HPO fraction (as opposed to BDOC levels of less than 5% for the biodegradation of the HPI fraction found in landfill leachate), thus making the HPI organic matter more refractory to bacterial degradation.

Table 6-3: Typical decrease in DOC values during the enhanced 4-Day BDOC experiment

Enhanced 4-day BDOC							
Fraction	d0	d1	d2	**d3**	d4	BDOC	NBDOC

HPO	6.9	5.0	4.0	**3.7**	4.8	3.2	3.7
HPI	6.1	5.7	4.2	**4.0**	5.0	2.1	4.0
TPI	9.4	7.0	6.8	**5.7**	7.2	3.8	5.7

A comparative analysis of the average % BDOC obtained using the original 6-day BDOC and the enhanced 4-day BDOC methods is displayed in **Figure 6-15**. BDOC values obtained from the enhanced 4-day BDOC method, which is accompanied by N and P nutrient additions, were somewhat higher compared to the BDOC values of the 6-day BDOC method (**Figure 6-15**). The BDOC from the enhanced-BDOC was on average 5.1% higher than BDOC of the same fraction when the original BDOC method was used. The average percentage BDOC obtained within the source water was 35.0% when using the 4-day BDOC method compared to 31.3% when following the original 6-day BDOC method. BDOC values obtained during a soil degradation study undertaken by McDowell *et al*. (2006) increased by between 6% and 13% when nutrients were added. Within the study of McDowell *et al*. (2006) where soil BDOC was investigated addition of 6 mL KH_2PO_4 (0.1%) and NH_4NO_3 (0.1%) were added to a 15 mL test solution having a DOC between 10 to 30 mg/L.



	HPO 6-Day	HPI 6-Day	TPI 6-Day	HPO 4-Day	HPI 4-Day	TPI 4-Day	5 mg/L NaAc	8 mg/L NaAc	10 mg/L NaAc
BDOC	36,8	31,8	32,1	41,9	34,3	35,3	80,3	87,8	89,1
NBDOC	63,2	68,2	67,9	58,1	65,7	64,7	19,7	12,2	10,9

Figure 6-15: Average percentage BDOC and NBDOC within the 6-day and enhanced 4-day BDOC methods

The addition of an easily biodegradable carbon source (glucose or sodium acetate) is often used during BDOC studies to ascertain the functioning of an assay, which provides information on active bacterial cultures and is therefore used as a control. In the case of the study of McDowell *et al*. (2006), between 88% and 94% of the carbon source in the sample control was removed by the bacteria after day 7. An investigation of the BDOC of sodium

acetate by Kaplan *et al*. (2004) resulted in BDOC values of between 89% and 94% being achieved during days 3 and 5 when heterotrophic bacteria attached to sand was used as an inoculum. From **Figure 6-15** the sodium acetate (NaAc) being the control, was degraded between 80.3% and 89.1% where larger sodium acetate concentrations (10 mg/L) resulted in a higher percentage or amount of organic carbon degraded. The high BDOC values of the control samples indicate adequate bacterial activity on the sand. Attermeyer *et al*. (2014) confirmed that increased DOC concentrations increase the growth of the bacteria thus resulting in increased DOC utilisation. It is clear from BDOC results depicted in **Figure 6-15** that microorganisms require easily biodegradable carbon as shown by a high percentage BDOC of sodium acetate.

Figure 6-16 portrays the percentage distribution of BDOC within the HPO, HPI and TPI fractions obtained from the 6-day and enhanced 4-day BDOC methods. Although comparable percentages of BDOC within these fractions were found using the two methods, the maximum turnover of bacterial carbon was achieved on day 3 of the enhanced method. This suggests that when carbon is the limiting factor (by addition of P and N) and the experimental temperature of the BDOC is increased, the carbon consumption by the bacteria is accelerated. These results correspond with that of another research investigation where increased bacterial growth efficiency (BGE) and increased DOC turnover were recorded at the end of the incubation period without the bacterial growth conditions being limited by the nutrients (Attermeyer *et al*., 2014).

Research has shown that the degradation of aromatic organic carbon necessitates more energy and therefore displays a smaller BDOC value compared to the degradation of LMW non-aromatic compounds (Hertkorn *et al*., 2002; Attermeyer *et al*., 2014). However, organic matter of HMW size has proven to be more bio-reactive, as demonstrated by Amon & Benner (1996). This conclusion was reached based on the increased growth and bacterial respiration of the HMW organic matter, confirming increased HMW organic carbon degradation compared to LMW compounds (Amon & Benner, 1996). In the present study, the HPO fraction was found to be more amenable to bacterial degradation (**Figure 6-14**). In addition, research performed by Hem & Efraimsen (2001) seems to suggest that assimilable organic carbon (AOC) is primarily associated with the HMW organic matter (HPO).

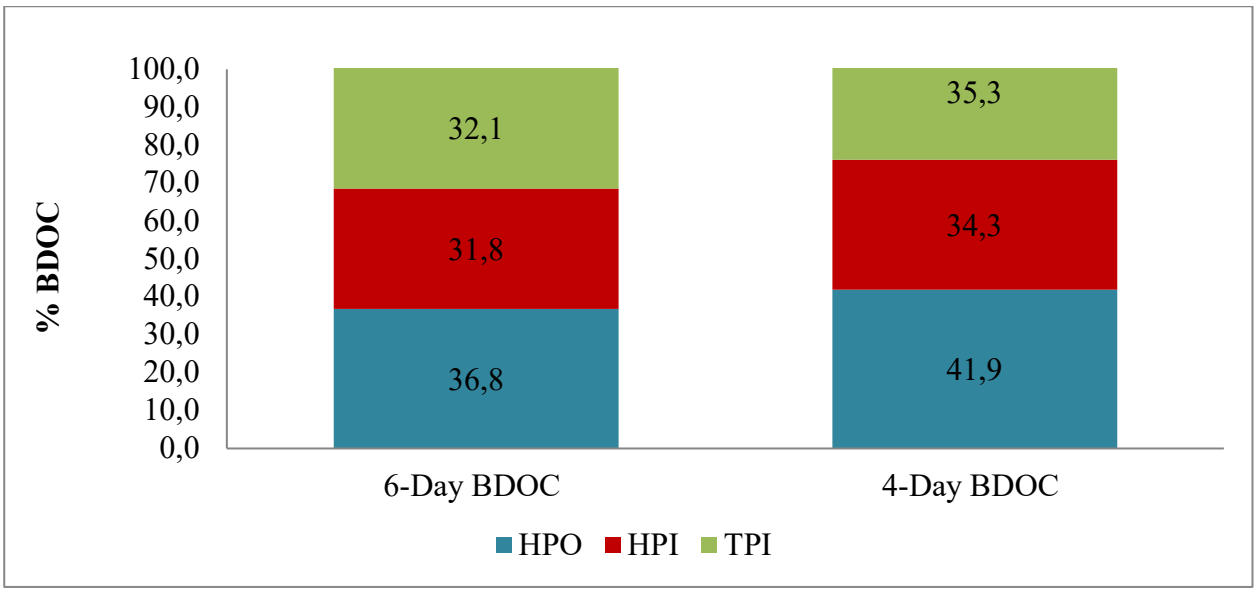


Figure 6-16: Percentage distribution of BDOC within the HPO, HPI and TPI fractions during the standard 6-day- and enhanced 4-day BDOC methods

In conclusion, by altering abiotic environmental conditions (i.e. temperature) and ensuring that DOC is the sole limiting nutrient (by addition of N and P) an improvement of the BDOC method was successfully carried out and was thus found to be more practical for application in full scale WTP operations. The enhanced 4-day BDOC analysis can be used to determine the removal efficiency of the bioavailable carbon by the water treatment plant. According to Block *et al*. (1993), the lesser the amount of the biodegradable organic components in the water after treatment the lesser the chance of bacterial regrowth in the distribution system.

The more rapid BDOC method can be used to ascertain bacterial carbon utilisation within 3 days and identifies the NOM fraction that is more easily biodegraded by the bacteria present in the distribution system. Identification of this specific NOM fraction is achieved by combining m-PRAM fractionation (producing the HPO, HPI and TPI NOM fractions) with the enhanced 4-day BDOC method to establish the NOM fraction that drives bacterial regrowth within the distribution pipelines. Although all three fractions are degraded by the bacteria, the HPO fraction was found to be responsible for the high biodegradability of the surface water, as reflected by the highest percentage BDOC measured in the HPO fraction (41.9%).

6.3.5 Trihalomethane formation potential (THMFP) analysis

The THMFP of the HPO, HPI and TPI NOM fractions obtained using the m-PRAM technique was investigated. The aim was to determine the NOM fraction that is more predisposed to form THMs during chlorination. Such an investigation is expected to assist with qualitative

characterization of the problematic NOM fraction found in the source water of the Rand Water treatment plant. **Tables 6-4** and **6-5** indicate the post m-PRAM fractionation UV_{254}, UV_{274} and pH measurements taken just before the samples were chlorinated with chlorine and incubated following the 7 day THMFP test. Except for the raw water samples from summer and autumn where a chlorine dosage of 12 mg/L was used, all samples were chlorinated with 10 mg/L of chlorine. These chlorine dosages, which were effected at the start of the incubation period, ensured a free chlorine residual concentration of between 3.5 to 5.2 mg/L at the end of the 7 day period (**Table 6-6**).

Table 6-4: Analyses performed on the NOM fractions of winter and summer samples

Fraction	UV_{254} (m^{-1})	UV_{274} (m^{-1})	pH
Vaal Dam source water – Winter 2017			
HPO	23.7	19.1	6.99
HPI	20.0	16.8	7.33
TPI	4.65	3.92	9.18
Full scale treated water – Winter 2017			
HPO	4.79	3.72	7.89
HPI	4.81	3.64	8.10
TPI	1.65	1.24	9.10
Vaal Dam source water – Summer 2017			
HPO	24.9	20.3	7.89
HPI	24.7	20.0	8.18
TPI	11.3	9.23	8.90
Full scale treated water – Summer 2017			
HPO	5.99	4.85	7.89
HPI	5.60	4.61	8.12
TPI	2.69	2.22	8.95

Table 6-5: Analyses performed on the NOM fractions of spring and autumn samples

Fraction	UV_{254} (m^{-1})	UV_{274} (m^{-1})	pH
Vaal Dam source water – Spring 2017			
HPO	35.4	28.7	7.7
HPI	34.0	27.2	7.7
TPI	33.9	27.3	8.6
Full scale treated water – Spring 2017			

HPO	9.9	7.9	7.8
HPI	9.6	7.8	7.8
TPI	9.2	7.4	8.6
Vaal Dam source water – Autumn 2017			
HPO	20.2	16.1	8.0
HPI	19.7	15.2	7.7
TPI	4.4	3.9	9.1
Full scale treated water – Autumn 2017			
HPO	5.1	3.1	7.7
HPI	4.4	2.9	7.8
TPI	2,8	1.3	8.9

From the results of the THMFP test it can be inferred that the HPO fraction for all the four seasons possessed the highest propensity to form THM during chlorination; the HPO was followed by the TPI and HPI fractions (**Table 6-7**). According to **Figure 6-17**, the THMFP concentration of the HPO NOM fraction present in the source water was found to be highest during the summer season, with a concentration of 224 µg/L being recorded. Furthermore, a decrease in the overall THMFP values was observed when moving from summer to spring seasons, with spring having the lowest average THMFP of 110 µg/L for the HPO NOM fraction (**Figure 6-16**).

Table 6-6: Chlorine consumption within the various fractions during the 7 day incubation period

Fraction	Cl_2 dosed (mg/L)	Cl_2 res. after 30 min. (mg/L)	Cl_2 res. after 2d (mg/L)	Cl_2 res. after 5d (mg/L)	Cl_2 res. after 7d (mg/L)	Cl_2 consumed after 7d (mg/L)
Chlorinated Vaal Dam source water – Winter 2017						
Not fractioned	10.0	9.2	5.2	6.8	3.8	6.2
HPO	10.0	8.4	5.0	4.8	4.2	5.8

HPI	10.0	11.2	9.4	6.6	5.2	4.8
TPI	10.0	10.0	7.2	6.90	4.4	5.6
Chlorinated full scale treated water – Winter 2017						
Not fractioned	10.0	9.1	5.2	4.8	4.1	5.9
HPO	10.0	9.2	7.0	4.6	3.9	6.1
HPI	10.0	8.2	9.4	7.0	4.8	5.2
TPI	10.0	8.0	7.3	6.4	4.4	5.6
Chlorinated Vaal Dam source water – Summer 2017						
Not fractioned	12.0	9.1	7.8	6.6	4.0	8.0
HPO	12.0	8.3	5.3	4.7	4.4	7.6
HPI	12.0	7.4	5.5	4.8	4.8	7.2
TPI	12.0	8.8	7.1	5.8	4.6	7.4
Chlorinated full scale treated water – Summer 2017						
Not fractioned	10.0	9.1	8.5	7.3	3.5	6.5
HPO	10.0	7.2	6.1	4.1	3.7	6.3
HPI	10.0	7.5	6.6	5.4	4.2	5.8
TPI	10.0	7.3	6.3	5.0	3.9	6.1

[Abbreviations: Cl_2 – free chlorine; res. – residual]

Table 6-7: THMFP results of the NOM fractions after the 7 day chlorination period

Fraction	Summer 2017	Autumn 2017	Winter 2017	Spring 2017
Chlorinated Vaal Dam source water				
HPO	224	189	116	110
HPI	164	139	100	82
TPI	172	146	106	87
Chlorinated full scale treated water				
HPO	156	116	98	78
HPI	104	65	60	44
TPI	110	81	70	58

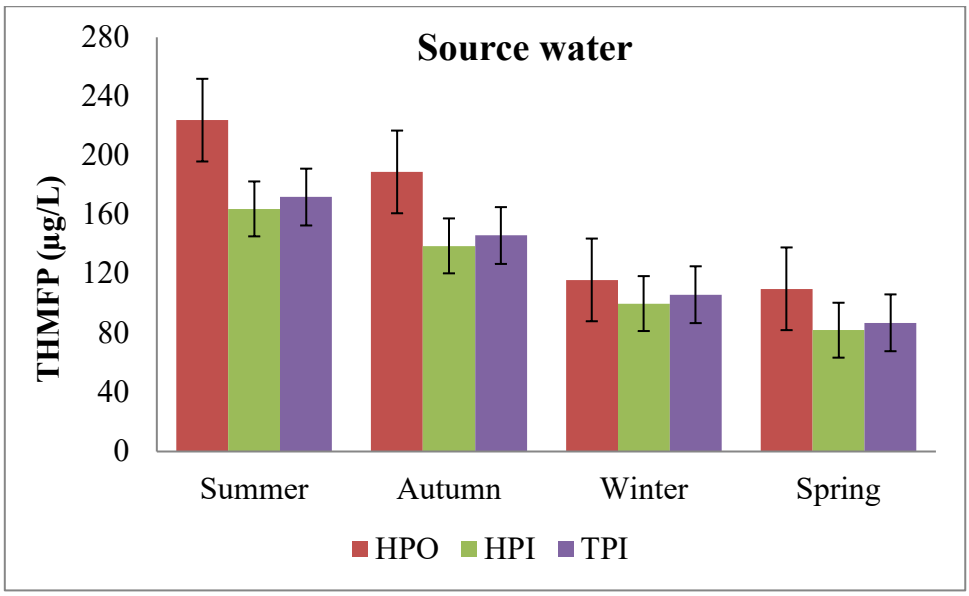


Figure 6-17: THMFP of the source water during the various season

The average THMFP from **Figure 6-18** for all four seasons is highest in the HPO fraction of the treated water. The THMFP in the HPO NOM had an average THMFP value of 224 µg/L from the surface water and 156 µg/L in water after full scale treatment, during summer (**Figures 6-17** and **6.18**). As shown in **Figure 6-18**, the THMFP of the treated water, which generally follows the seasonal trend summer > winter > autumn > spring, correlates well with trends reported in the literature (Golea *et al*., 2017). A study performed by Awad *et al*. (2017) has revealed that the THMFP of river water samples was also higher during wet summer seasons as highlighted by a THMFP of 217 µg/L. High THMFP values (187 µg/L) were reported for the wet summer season compared to the dry season (winter) where an average THMFP value of 107 µg/L was recorded. According to data presented in **Figure 6-19**, some of the THM precursors were removed by the treatment plant; this is confirmed by decreased THMFP values associated with all the three fractions obtained from the treated water.

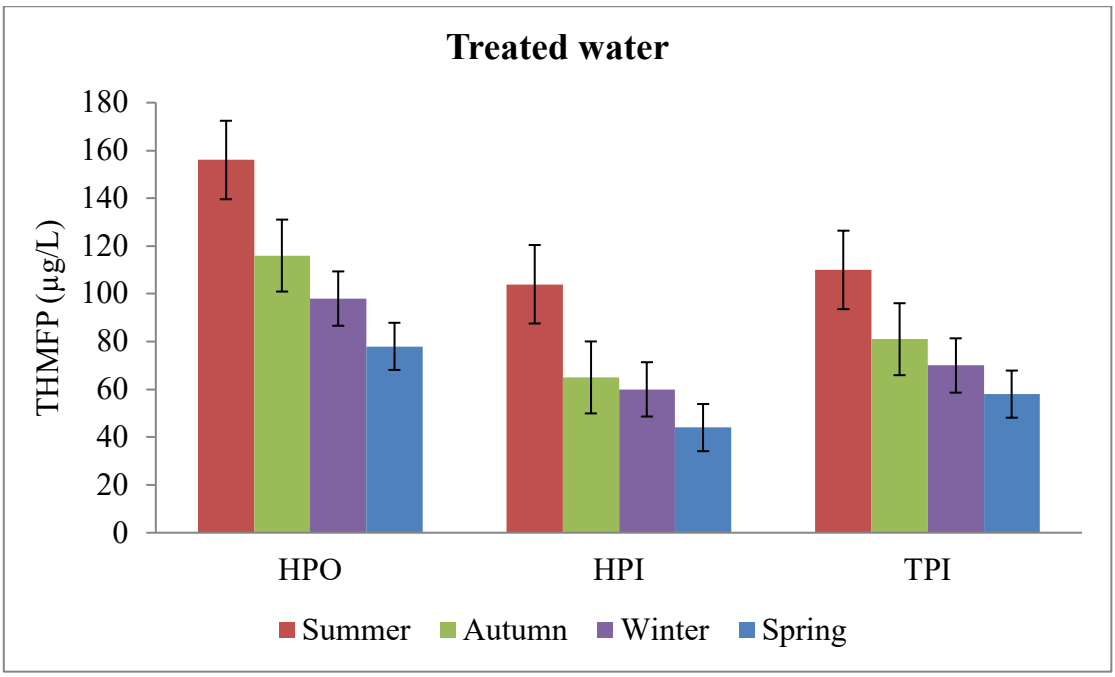


Figure 6-18: THMFP of the treated water during the various seasons

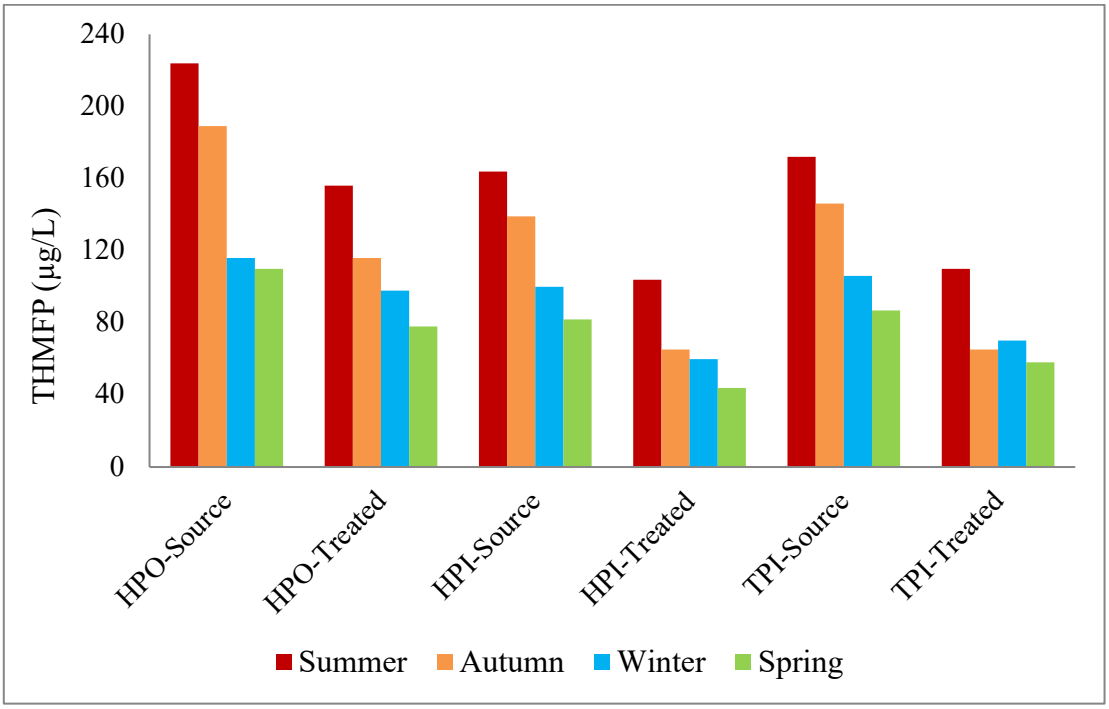


Figure 6-19: Summary of THMFP on source water and full scale treated water fractions during summer, winter, spring and autumn

Furthermore, THMFP results obtained from this study are in agreement with other studies where it was proven that compounds with high aromaticity are largely responsible for THM formation emanating from the HPO fraction (Lu *et al*., 2009; Golea *et al*., 2017). Hydrophobic compounds of HMW often result in increased THMFP relative to the LMW protein organic matter (Hassouna *et al*., 2014; Awad *et al*., 2015). Samples with large amounts of aromatic

organic compounds have a high chlorine demand (Abdullah *et al*., 2009; Awad *et al*., 2015) and show a strong positive correlation between the SUVA and THMFP (Parsons *et al*., 2004; Abdullah *et al*., 2009).

As shown in **Figure 6-20**, the average percentage reduction in the THMFP for all fractions during all four seasons was found to be 37.4%. According to Zainudin *et al*. (2018), 27.2% of THMFP was removed using $FeCl_3$ as a coagulant during the coagulation/flocculation steps. As illustrated in **Figure 6-20**, the THMFP removal of the HPO fraction is the lowest (27.7%) compared to the THMFP of the HPI and TPI fractions. Although **Figure 6-5** inidicate some removal of the HPO NOM fraction **Chapter 5** illustrated that not all of the HPO NOM was effectively removed by the water treatment process (**Chapter 5: Figure 5-2**) and it was also found that the HMW HPO fraction was responsible for the THMs formed, especially chloroform during summer months (**Chapter 5: Figure 5-5**). **Figure 6-21** is a summary of the overall percentage distribution of the THMFP of the HPO, HPI and TPI NOM fractions and also shows that the HPO fraction of the treated water has the highest propensity to form THMs.

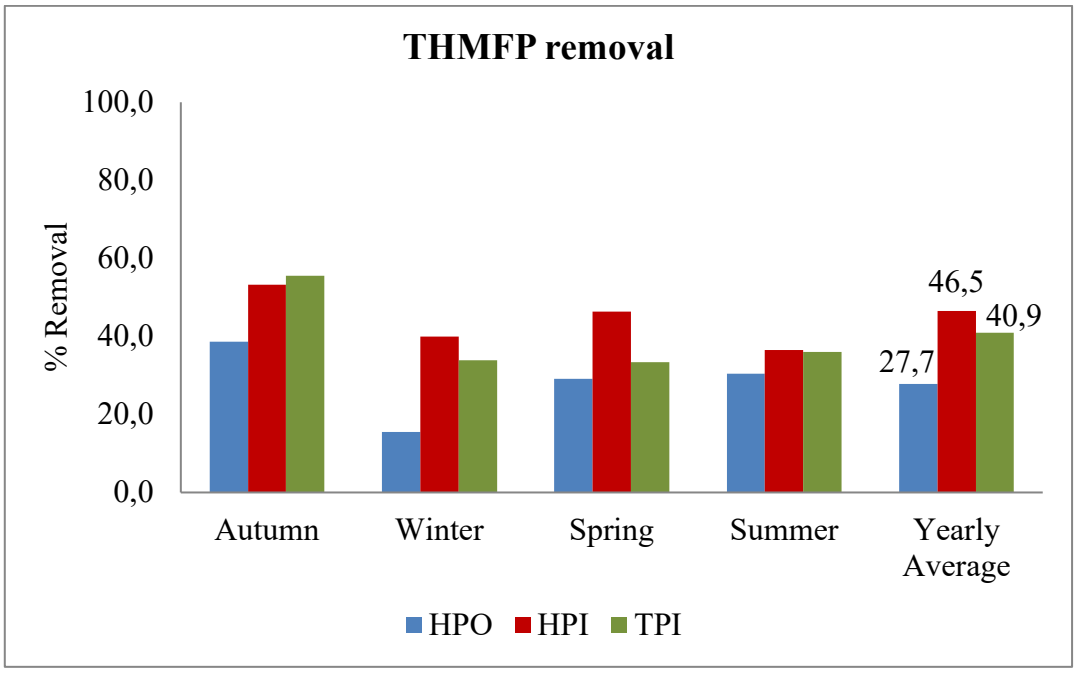
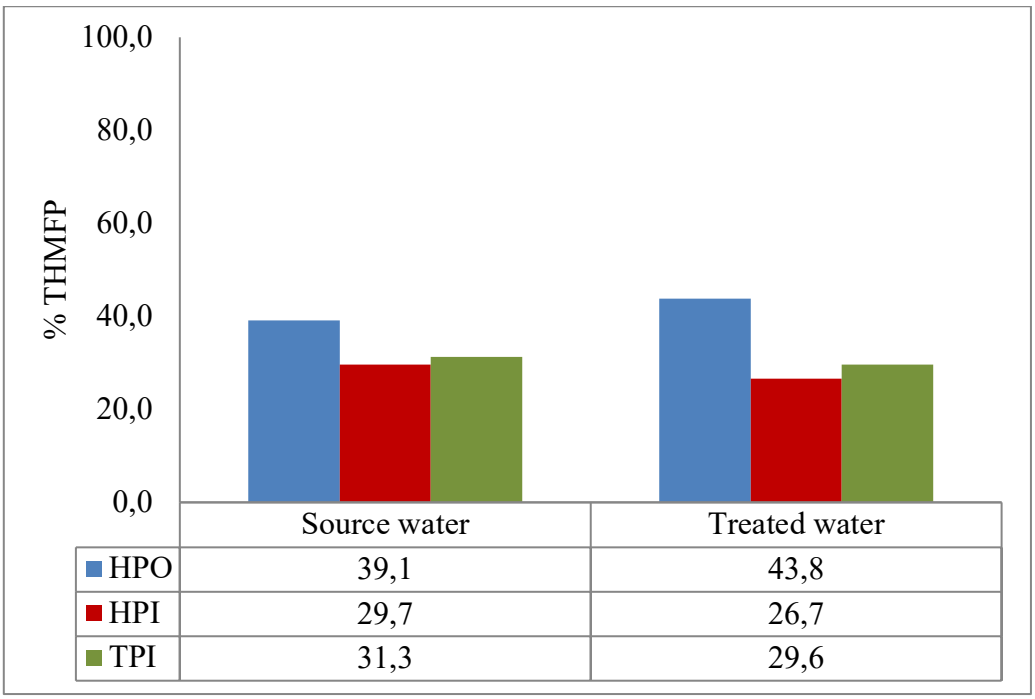


Figure 6-20: Percentage THMFP removals after full scale conventional water treatment



	Source water	Treated water
HPO	39,1	43,8
HPI	29,7	26,7
TPI	31,3	29,6

Figure 6-21: Distribution of the percentage THMFP within the HPO, HPI and TPI fractions within the source and final treated water

Figure 6-22 is a summary of the results from the modified-PRAM fractionation, enhanced BDOC and the THMFP analyses, forming part of the NOM characterization protocol when investigating the HPI, HPO and TPI NOM fractions. Although a similar distribution of the HPO, HPI and TPI NOM in the source water sample was observed, the percentage BDOC and THMFP of the HPO fraction was found to be higher than those of the HPI and TPI fractions. Therefore, besides being more amenable to bacterial degradation, it can also be concluded that the HPO NOM fraction has the highest potential to form THMs in the final drinking water if not effectively removed by the WTP. Various studies suggest that the size exclusion chromatographic (SEC) characterization of the HPO, HPI and TPI fractions follow the order HPO > TPI > HPI (Croué, 2004; Labanowski & Feuillade, 2009). Therefore, the HPO NOM and the HPI organic is associated with the respective high molecular weight (HMW) and low molecular weight (LMW) NOM's. The BDOC and THMFP order of HPO > TPI > HPI, which is illustrated in **Figure 6-22**, implies that the HPO fraction is much more prone to biodegradability and possess a higher potential to form THMs. So, it suffices to mention that the HPO has been identified as the problematic NOM fraction found in the water samples sourced from the Vaal Dam.

The PRAM method was found in this project to be very convenient in performing a treatability assessment of NOM. In particular, it was possible to infer from PRAM the distribution of the polar and non-polar fractions, which bears witness to the dominant fraction appearing in the

source water and by extension whether the NOM fraction had indeed been removed. As shown in **Figure 6-22**, the high occurrence (i.e. 35%) of HPO NOM shows that this type of source water has a high propensity to form THMs, which is confirmed by a THMFP of 39.1%.

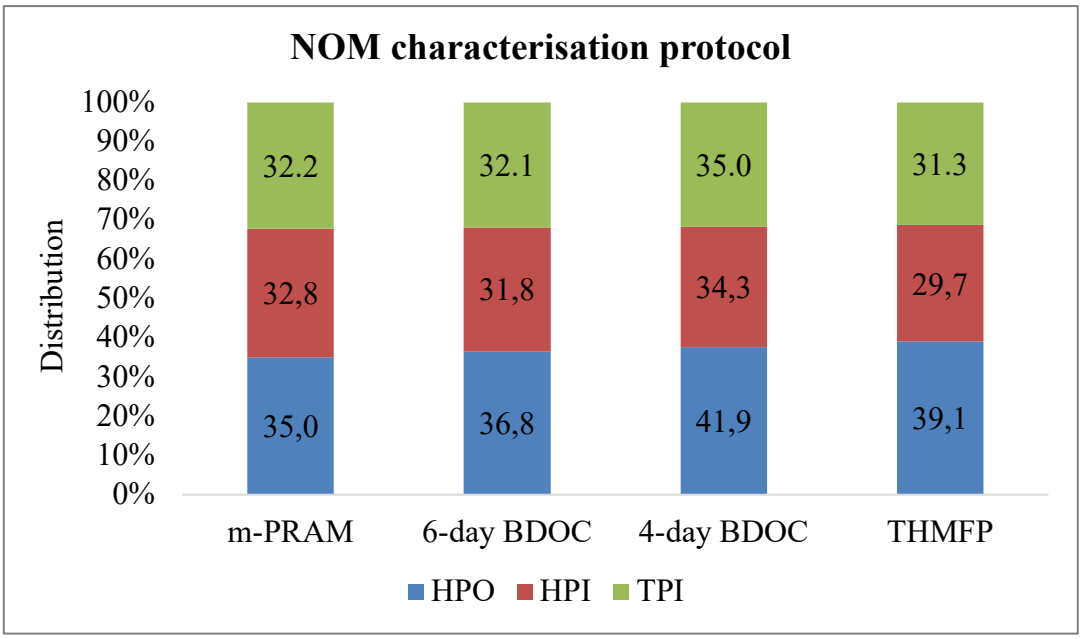


Figure 6-22: Summary of results of the NOM characterization protocol (m-PRAM, enhanced-BDOC and THMFP) for the source water samples

According to PRAM fractionation results summarised in **Figure 6-23**, the HPO NOM fraction that remained in the final treated water following full scale treatment constitutes 31.6% of the organic matter. With a THMFP of 43.8%, this HPO fraction possesses the highest predisposition towards the formation of THMs. Although the polar (HPI) fraction constitutes only 37.8% of the organic matter (due to this fraction not being removed by the treatment), the THMs most likely to be produced from this fraction has the lowest THMFP of 26.7%. It is noteworthy that from PRAM fractionation and THMFP these fractions seem to point to the largest THMFP occurring within the HPO fraction.

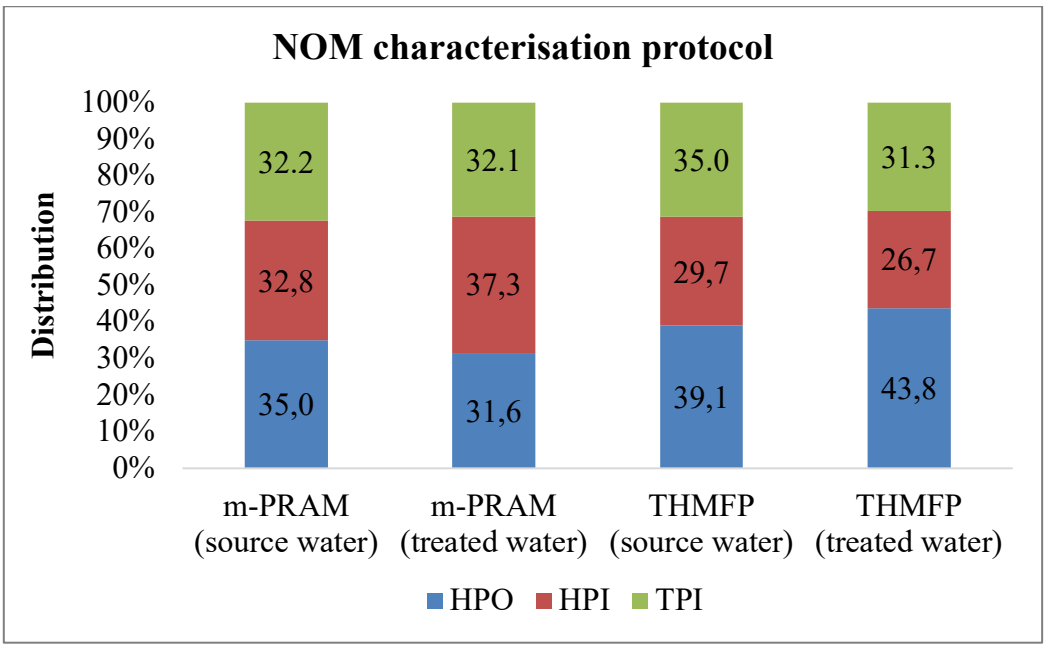


Figure 6-23: Summary of PRAM and THMFP results in the source and final treated water

6.3.6 Fluorescence excitation emission (FEEM) analysis and THMFP

The last step in the NOM characterization protocol involves FEEM analysis of the fractionated NOM water assessed during the 7 day THMFP investigation. The sampling analysis flow diagram of the NOM fractionation (m-PRAM) and characterization (THMFP, FEEM) is presented in **Figure 6-24**. It was envisaged that results derived from these analyses would assist in establishing the treatability of the various NOM fractions. The simultaneous determination of THMFP and FEEM investigates the change in the fluorescence intensity of the individual NOM fractions (HPO, HPI and TPI) during the chlorination process. The FEEM was recorded using a Horiba (AquaLog Inc. USA) spectrometer with FEEM parameters: excitation from 240 to 600 nm at 2 nm steps, emission from 247 to 825 nm at 4 nm steps, 2 nm bandwith and an integration time of 1 second. Quantification of the FEEM spectra was performed using the fuorescence regional integration (FRI) method where the area volume (Pi,n) of each region is calculated (Chen *et al*., 2003). The fluorescence intensity was separated into five regions each representing a specific compound group; protein-like (Region I and II), fulvic-like (Region III), microbial by-product-like (Region IV) or humic-like (Region V) as demonstrated in **Table 6-8**.

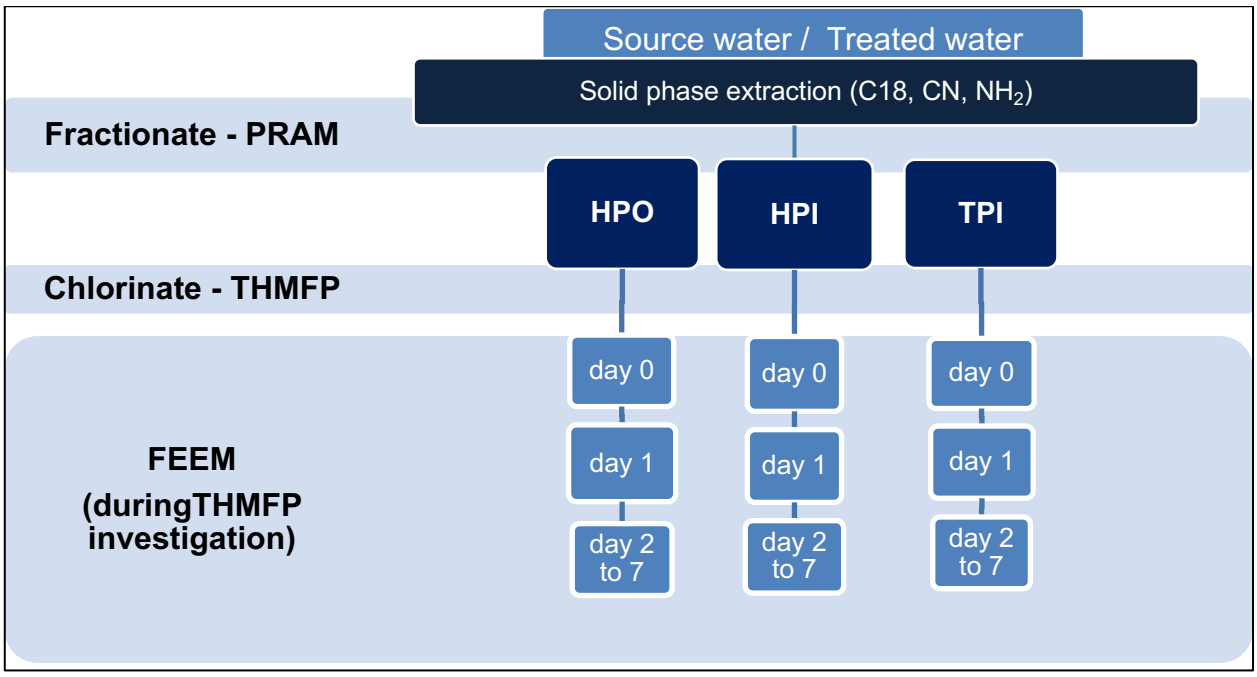


Figure 6-24: Flow diagram for m-PRAM-THMFP-FEEM analyses for NOM characterization

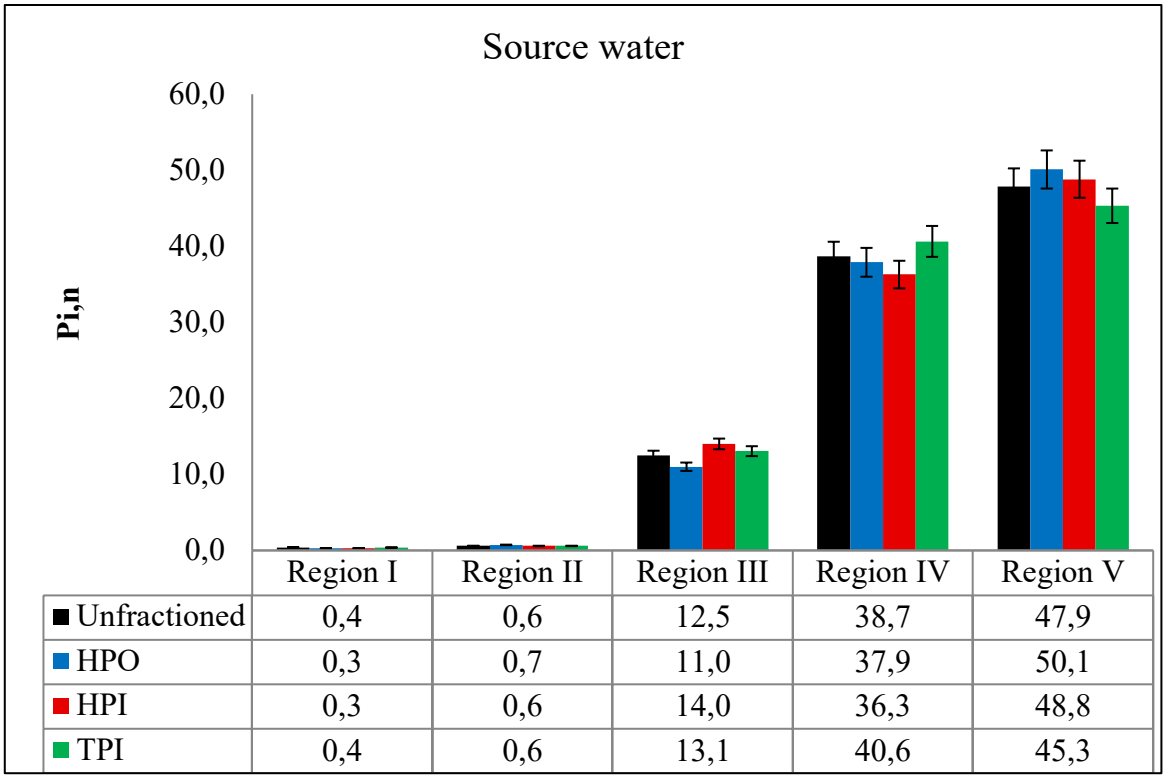
Table 6-8: Region location and description of the fluorophores for the fluorescence regional intergration (FRI) (Chen *et al.*, 2003)

Region	Excitation wavelength range (nm)	Emission wavelength range (nm)	Component description
Region I	220 - 250	280 - 332	Protein-like Tyrosine-like
Region II	220 - 250	332 - 380	Protein-like Tryptophan-like
Region III	220 - 250	380 - 580	Fulvic acid-like
Region IV	250 - 470	280 - 380	Microbial by-product-like
Region V	250 - 470	380 - 580	Humic acid-like

The area volume (Pi,n) of each region in the FEEM spectra of the source and treated bulk water (unfractioned), HPO, HPI and TPI fractions is presented in **Figures 6-25** and **6-26**. The fluorescence intensities decreased in the order Region V > Region IV > Region III > Region II > Region I in the unfractioned bulk source and full scale treated water (**Figures 6-25** and **6-26**). It can therefore be concluded that Vaal Dam surface water is characterized

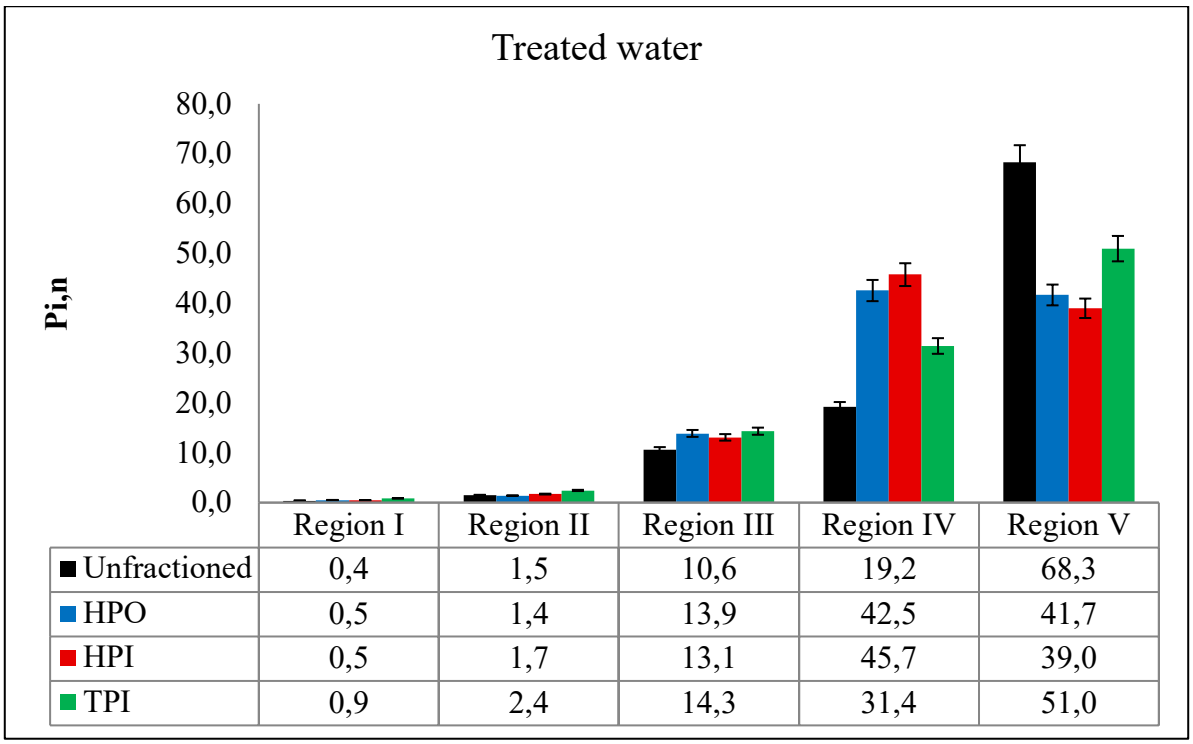
by high humic, microbial by-product and fulvic components as manifested by high proportions in Regions V, IV and III.

Figure 6-25 portrays a small quantity of proteinaceous material with a low intensity of the protein-like fluorophores (Regions I and II). Higher intensities in Region II (aromatic proteins) in the treated water is observed due to an increase in free amino acids after full scale treatment (**Figure 6-26**). Overall, a reduction of the humic acid-like fluorophores (Region V) is notable in the HPO and HPI fractions after full scale treatment when comparing the area volume of Region V in the source water to the area volume of Region V in the treated water (**Figures 6-25** and **6-26**). The UV absorbance spectra of the source and treated water presented in **Figures 6-27** and **6-28**, shows higher UV_{254} absorbancies in the HPO fractions compared to the bulk water (unfractioned), HPI and TPI fractions.



	Region I	Region II	Region III	Region IV	Region V
Unfractioned	0,4	0,6	12,5	38,7	47,9
HPO	0,3	0,7	11,0	37,9	50,1
HPI	0,3	0,6	14,0	36,3	48,8
TPI	0,4	0,6	13,1	40,6	45,3

Figure 6-25: Typical FRI results of the FEEM matrix on fractioned (HPO, HPI, TPI) and unfractioned Vaal Dam source water



	Region I	Region II	Region III	Region IV	Region V
Unfractioned	0,4	1,5	10,6	19,2	68,3
HPO	0,5	1,4	13,9	42,5	41,7
HPI	0,5	1,7	13,1	45,7	39,0
TPI	0,9	2,4	14,3	31,4	51,0

Figure 6-26: Typical FRI results of the FEEM matrix on fractioned (HPO, HPI, TPI) and unfractioned treated water (full scale sand filtration)

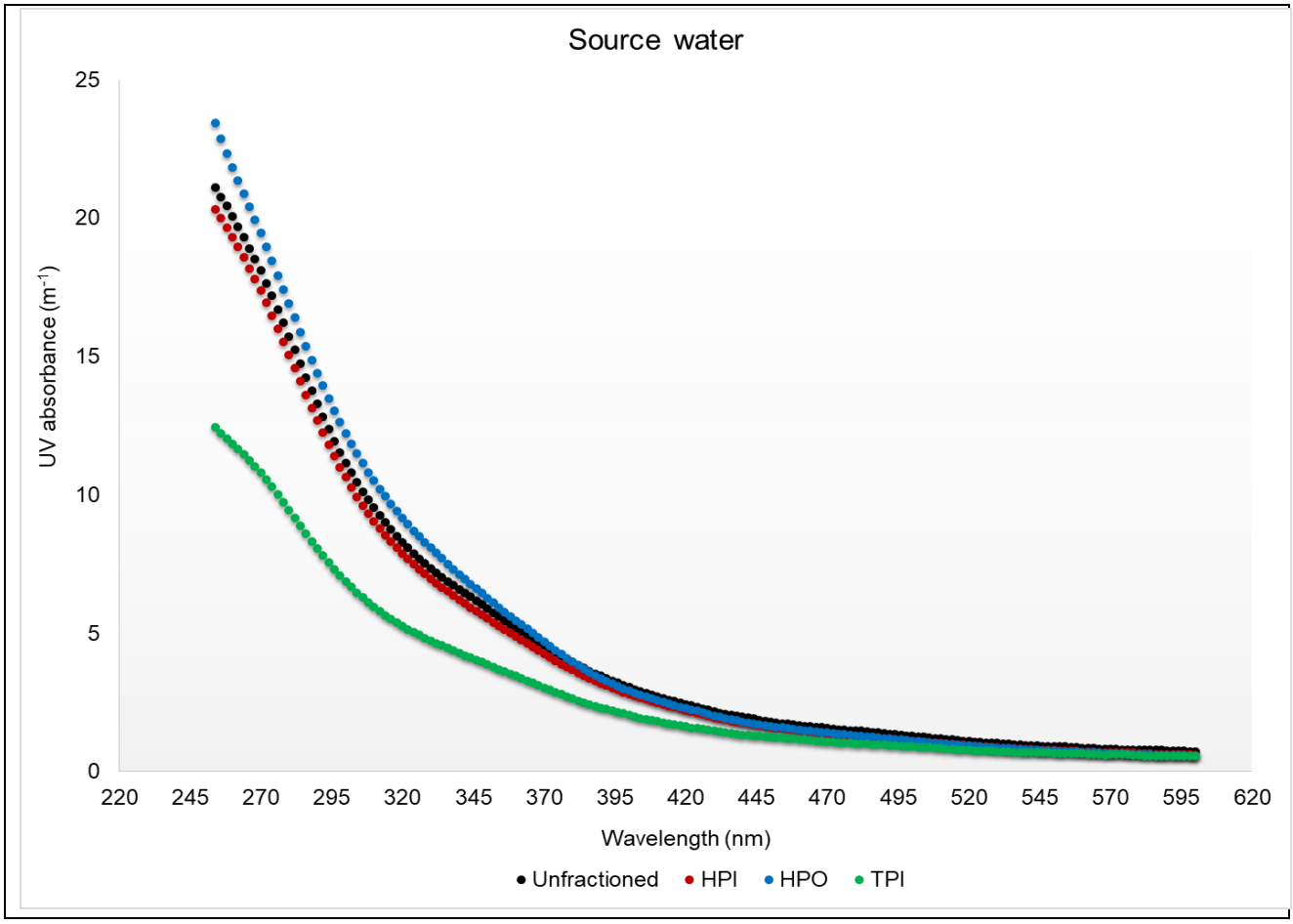


Figure 6-27: UV absorbance spectra of the source water

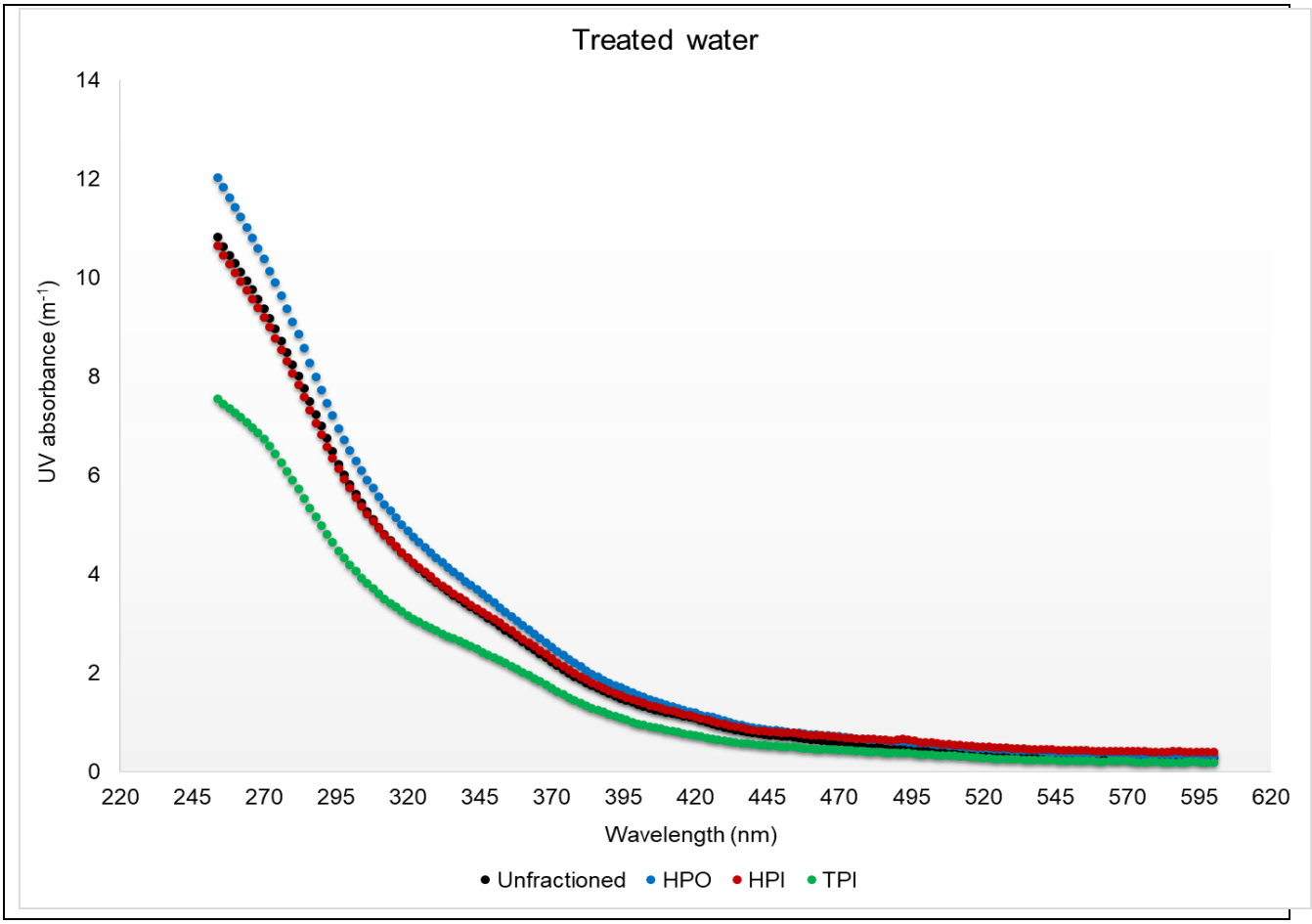


Figure 6-28: UV absorbance spectra of the treated water

Figure 6-29 and **6-30** depicts the area volumes (Pi,n) of each region in the excitation-emission matrix before chlorination (HPO, HPI, TPI) and after chlorination (on day 7). These area volumes were calculated according to Chen *et al*. (2003). In **Figure 6-29** the fulvic-like components of the source water was only reduced in the HPI NOM fraction as shown by a small reduction in the area volume of Region III, during the 7 day chlorination experiment. The humic acid-like components (Region V) were more prominently reduced in the HPO fraction of the source and treated water after chlorination (**Figures 6-29** and **6-30**). The reductions in fluorescence intensities of the humic-like components in the HPO fraction and the fulvic-like components in the HPI fraction was caused by the addition of chlorine on day 0 of the THMFP experiment. The measurement of FEEM before and after chlorination in the THMFP study evaluated the compound groups that are likely contributing to the THMs formed. It can be concluded that chlorine would typically react with humic substances as demonstrated in Zhang *et al*. (2009).

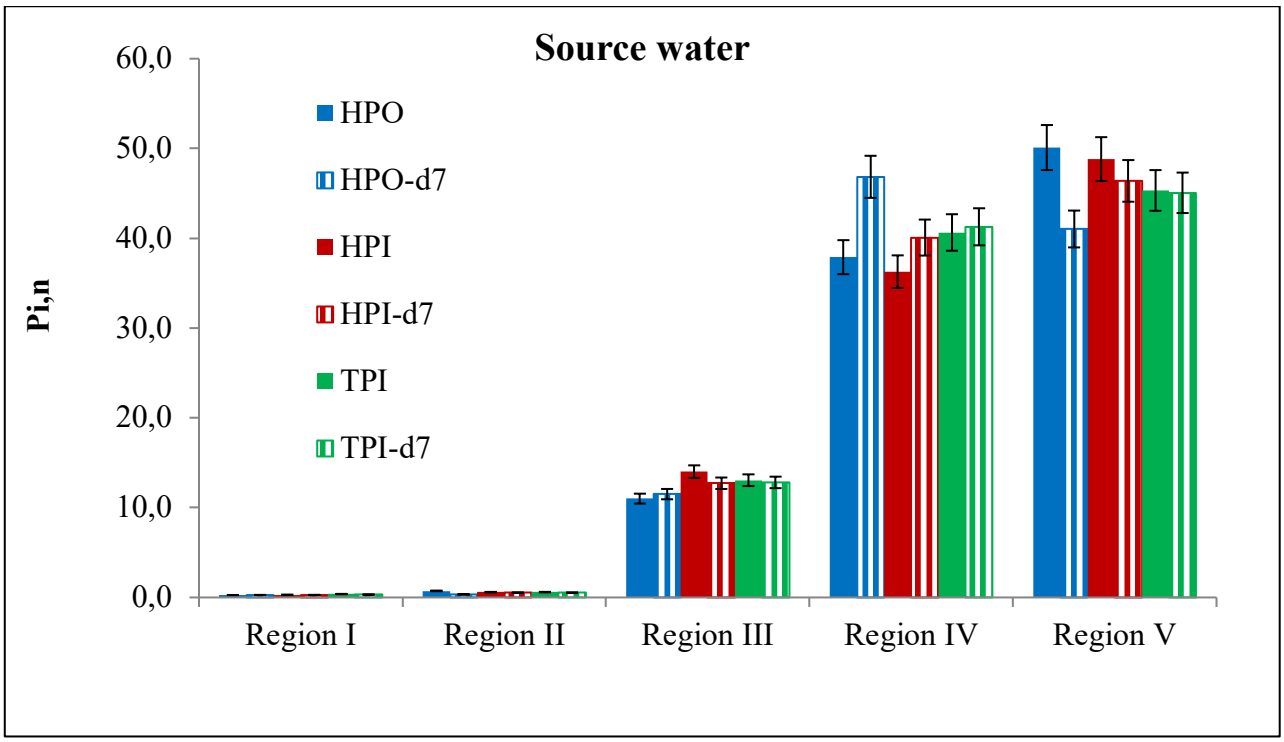


Figure 6-29: FRI results of the NOM fractions in source water before and after chlorination

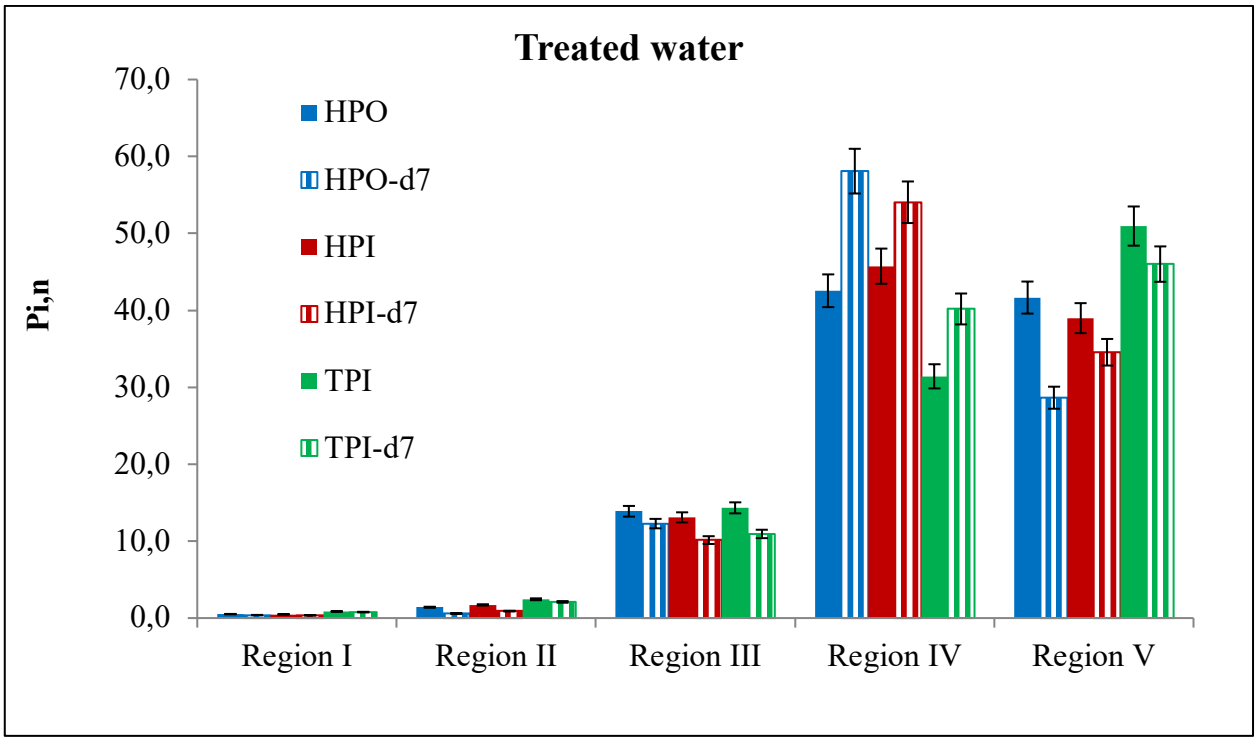


Figure 6-30: FRI results of the NOM fractions in full scale treated water before and after chlorination

Figure 6-31 entails the percentage reduction of the area volume in the different regions of the full scale treated water that occurred during the 7 days of the THMFP experiment. Chlorination reduced the protein-like, fulvic acid-like and humic acid-like fraction from the

HPO, HPI and TPI fractions. As seen in **Figure 6-31** the Regions II and V area volumes were reduced by 58% and 31%, respectively for the HPO fraction. With the HPI fraction chlorination decreased the area volume of Region II by 47% and the area volume of Region III by 23%. The protein-like (Region II) and fulvic acid-like (Region III) components' area volumes in the TPI fraction were reduced by 14% and 24%, respectively. These results demonstrated a reduction of the fluorescence intensities in the specific regions after disinfection, suggesting that chlorine would react with aromatic proteins (tryptophan-like) in both the HPO and HPI fractions. Chlorine can also react with the humic acid-like material in the HPO NOM and with the fulvic acid-like components in the HPI fraction. These results concur with the study performed by Li *et al*. (2017) which proved that chlorine is more likely to react with the humic acid-like material in the HPO NOM and with the fulvic acid-like material within HPI NOM. Therefore, due to the increased reactivity of humic acids with chlorine, increased halogenated DBP formation should be expected from the HPO NOM (Kitis *et al*., 2002; Li *et al*., 2017). This was confirmed in this thesis whereby the HPO NOM fraction has shown to have a greater tendency to form THMs (**Section 6.3.5),** which was also revealed in **Section 5.3.2** (**Chapter 5**) demonstrating that HMW HPO NOM was the leading precursor in the formation of THMs in the final water.

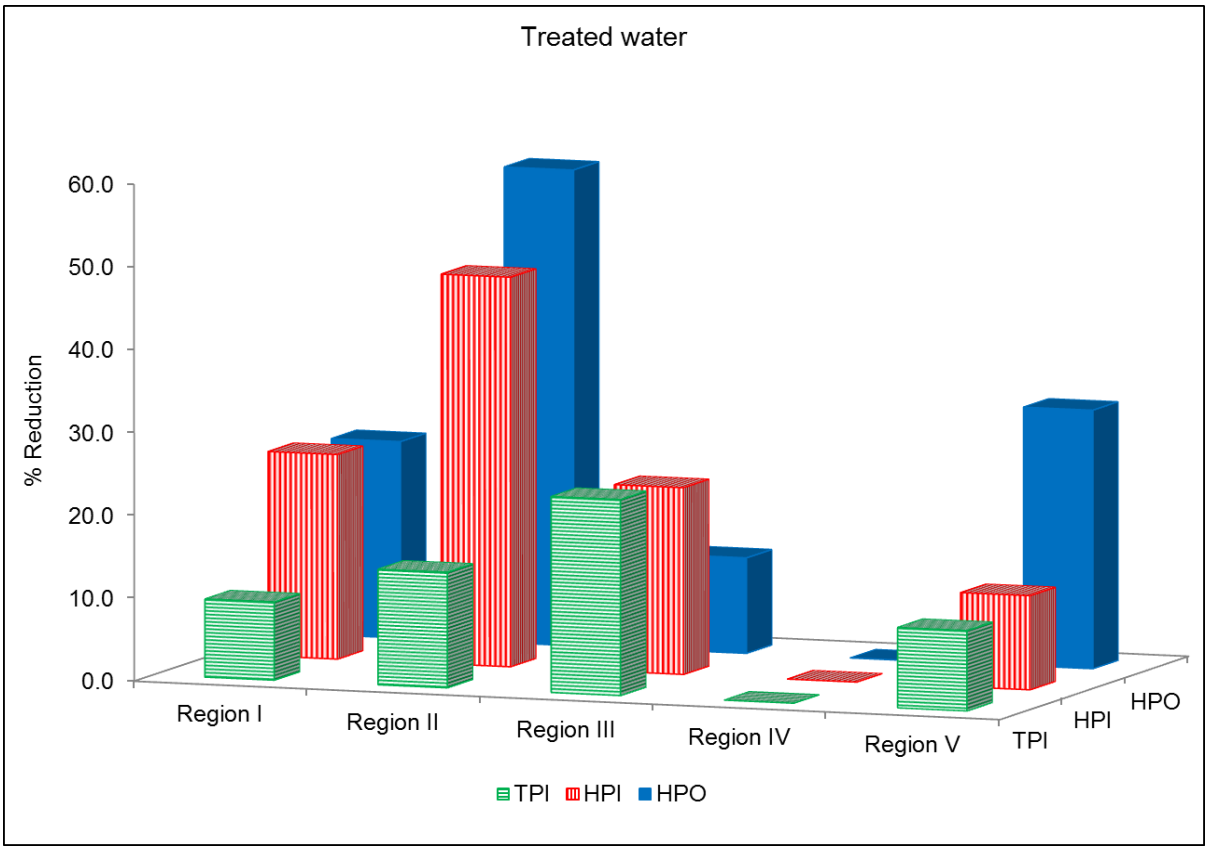


Figure 6-31: Percentage reduction of the area volumes in each fraction after disinfection

The FEEM contour plots obtained during days 0 to 7 of the THMFP investigation are presented in **Figures 6.32** to **6.39**. As shown in **Figure 6.32**, the source of the NOM compound found in the source water samples was of allochtonous (terrestrial) organic carbon input. This was demonstrated by the excitation and emission intensity of the NOM fluorophores of the source water that was concentrated within the excitation emission wavelength of 260 nm: 420 nm illustrating humic acid-like material (**Figures 6.32**, **6.34**, **6-36** and **6-38**). Fluorophores at this emission and excitation wavelengths are characterized as humic-like compound groups, implying that the nature of organic matter in the Vaal Dam source water is mostly humic-like material (Coble *et al*., 2014; Matilainen *et al*., 2011).

When comparing the FEEM contour plots of the HPO source water before chlorination to the FEEM contour plots on day 7, a decrease in the intensity of the humic-like components was observed (**Figure 6-34** and **6-35**). A similar decrease of the fluorescence intensity of the humic-like matter was observed in the HPI and TPI fractions during the 7 day THMFP study, although the reduction was not that prominent when comparing **Figures 6-37** and **6-39** to **Figure 6-35**. These humic-like compounds (of HMW) often result in increased THMFP when compared with protein-like (LMW) organic matter (Awad *et al*., 2015). Li *et al*. (2017) has also suggested that humic-like components are the major precursors of halogen-containing DBPs (THMs). This has been demonstrated in this study, where HPO NOM was the major THMs precursor given the high THMFP.

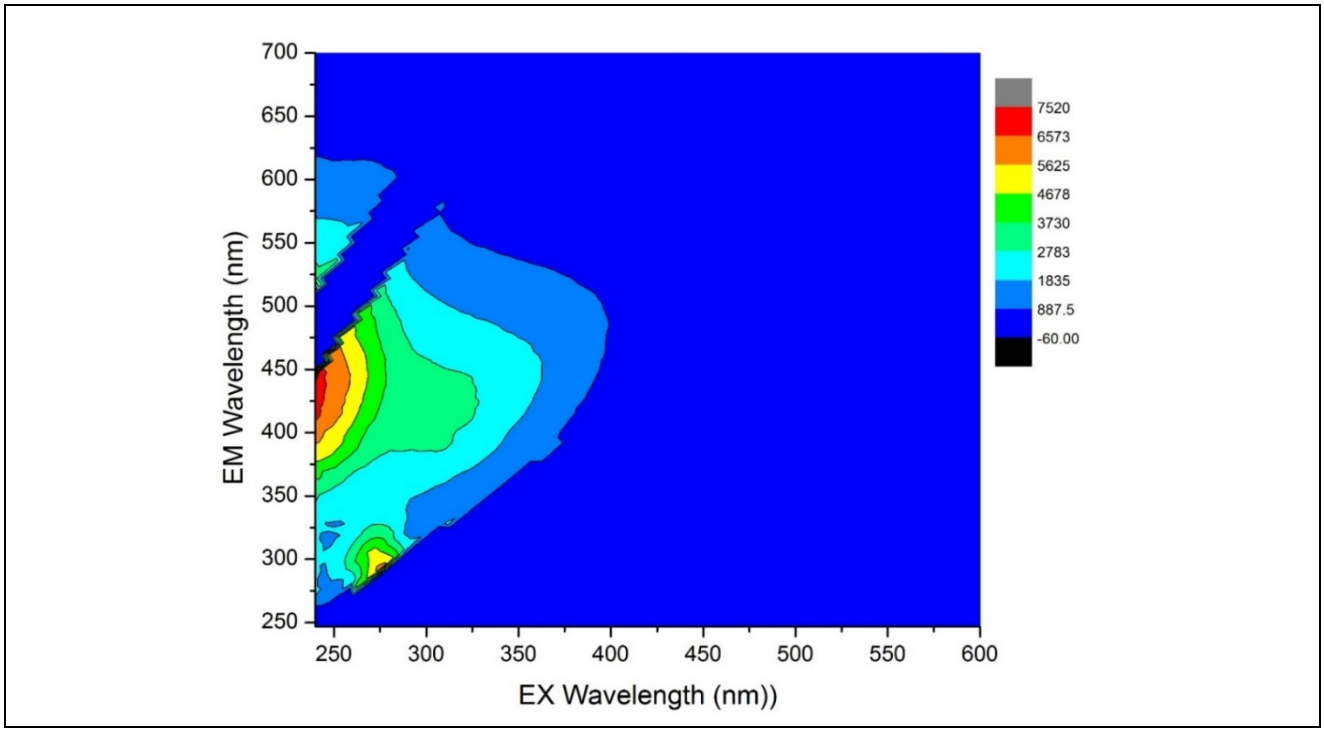


Figure 6-32: FEEM of the bulk source water before THMFP test

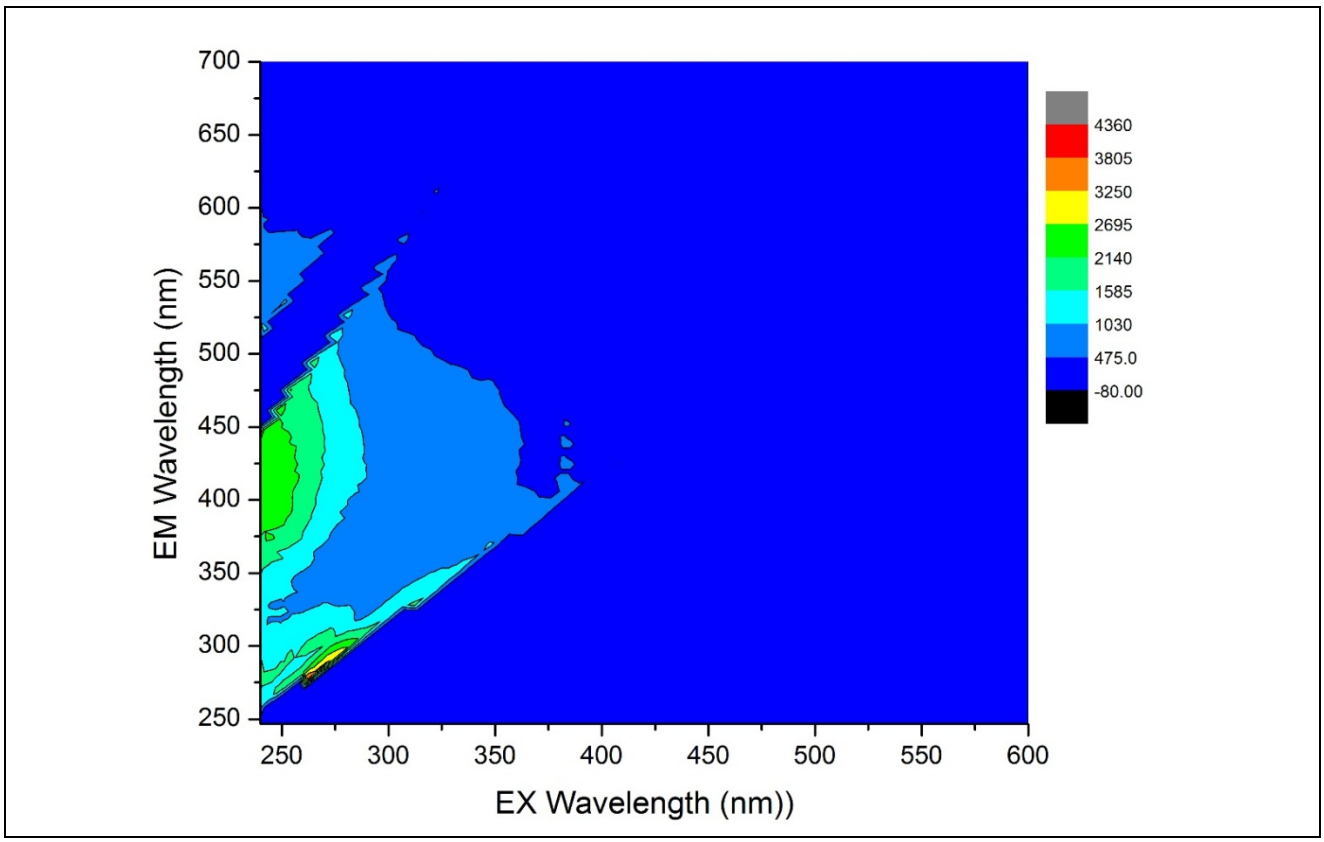


Figure 6-33: FEEM of the bulk source water on day 7 of the THMFP test

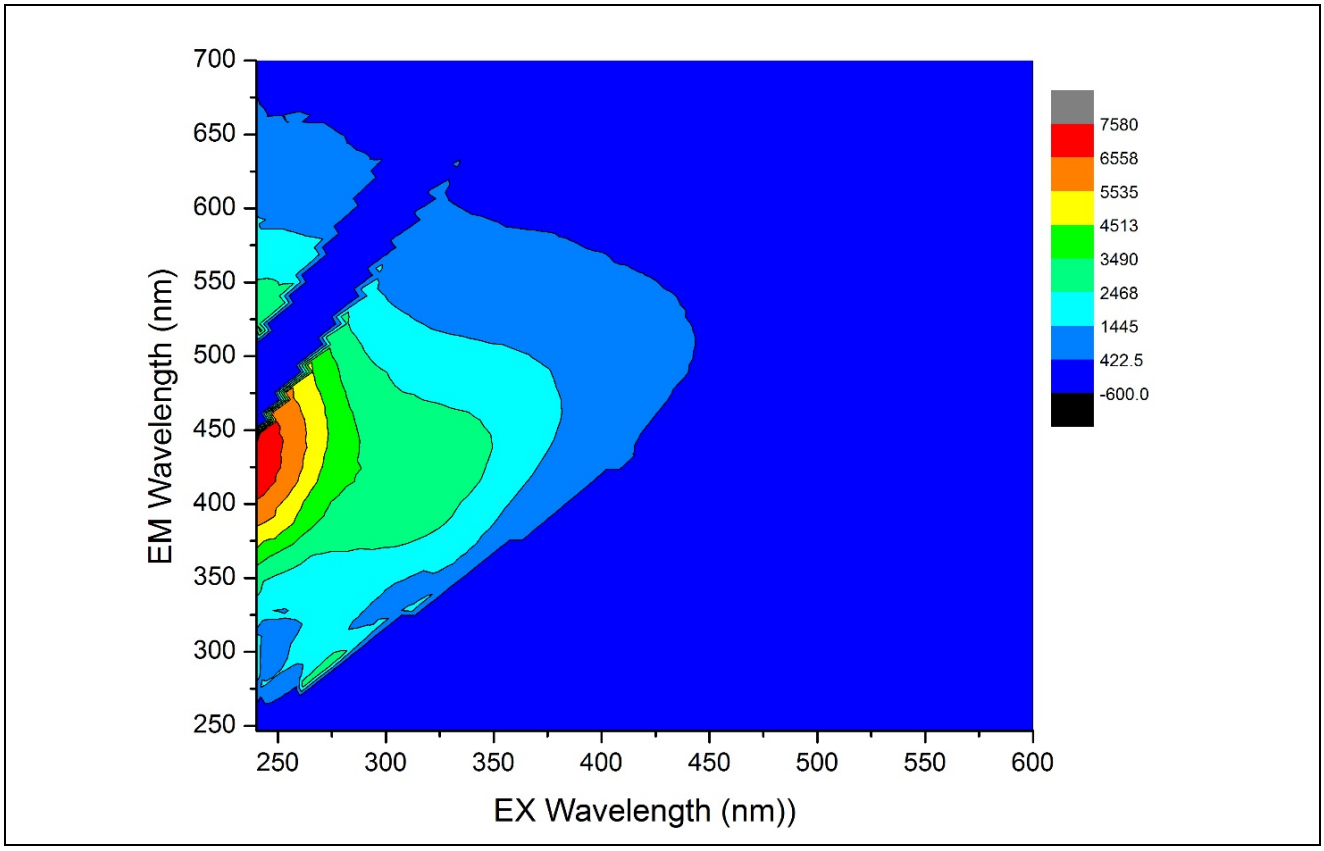


Figure 6-34: FEEM of the source water HPO fraction before THMFP test

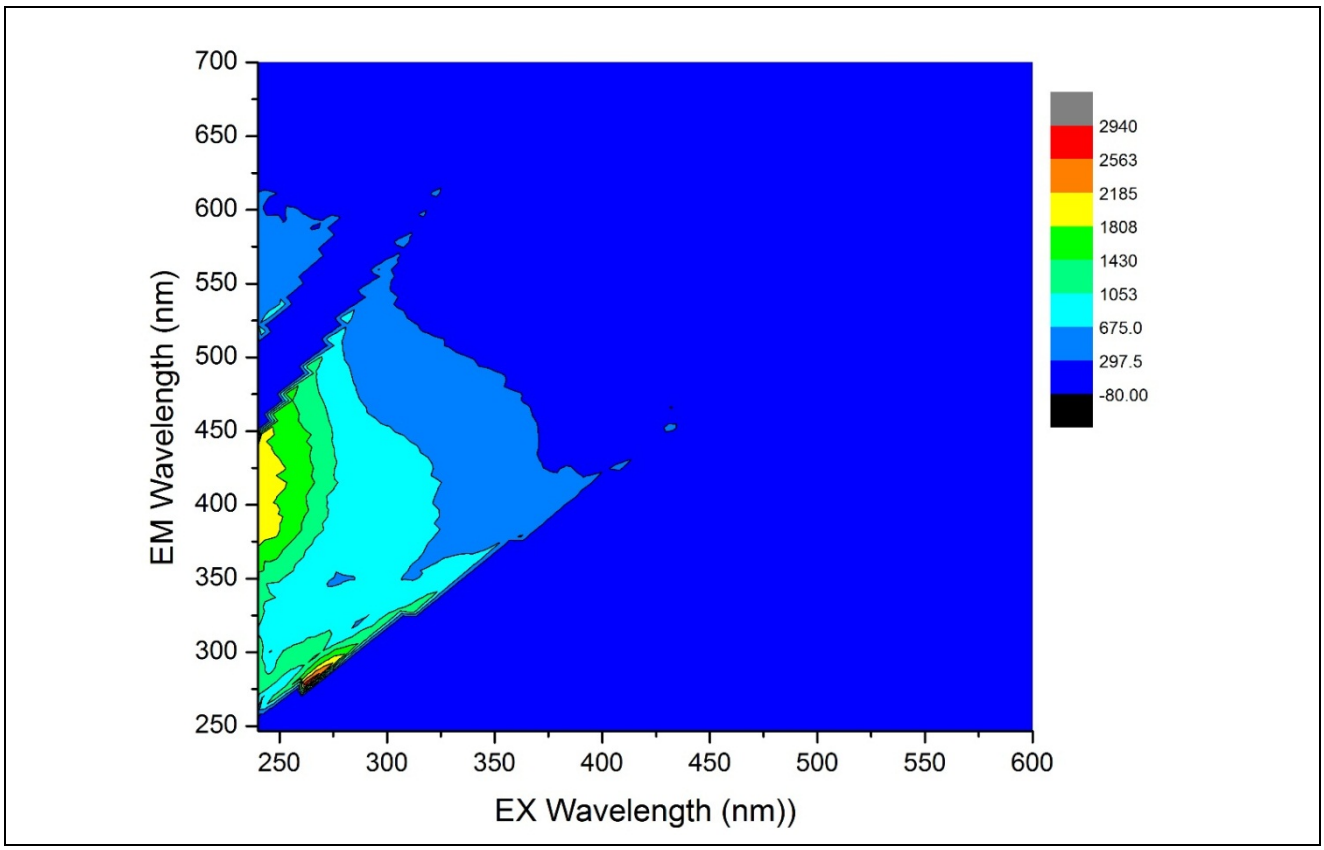


Figure 6-35: FEEM of the source water HPO fraction on day 7 of the THMFP test

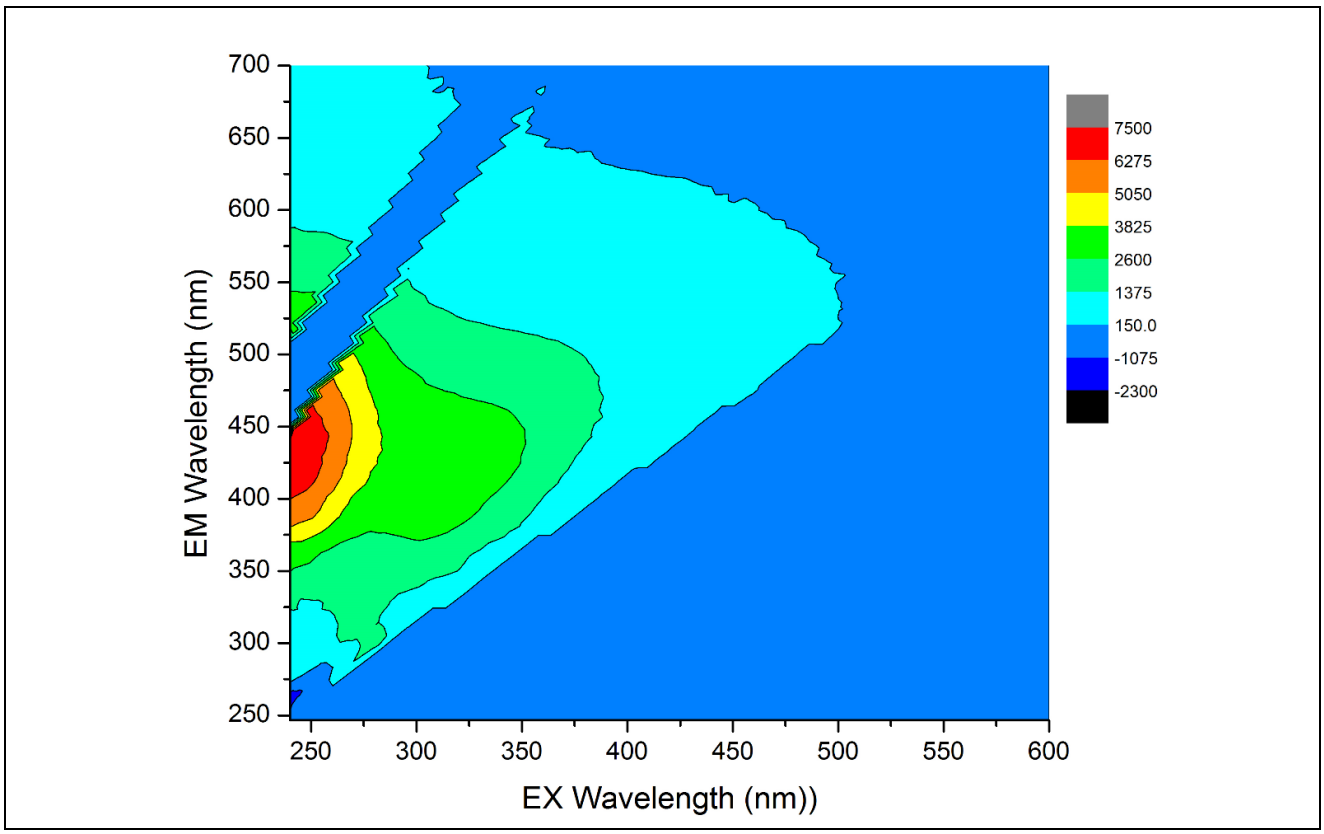


Figure 6-36: FEEM of the source water HPI fraction before THMFP test

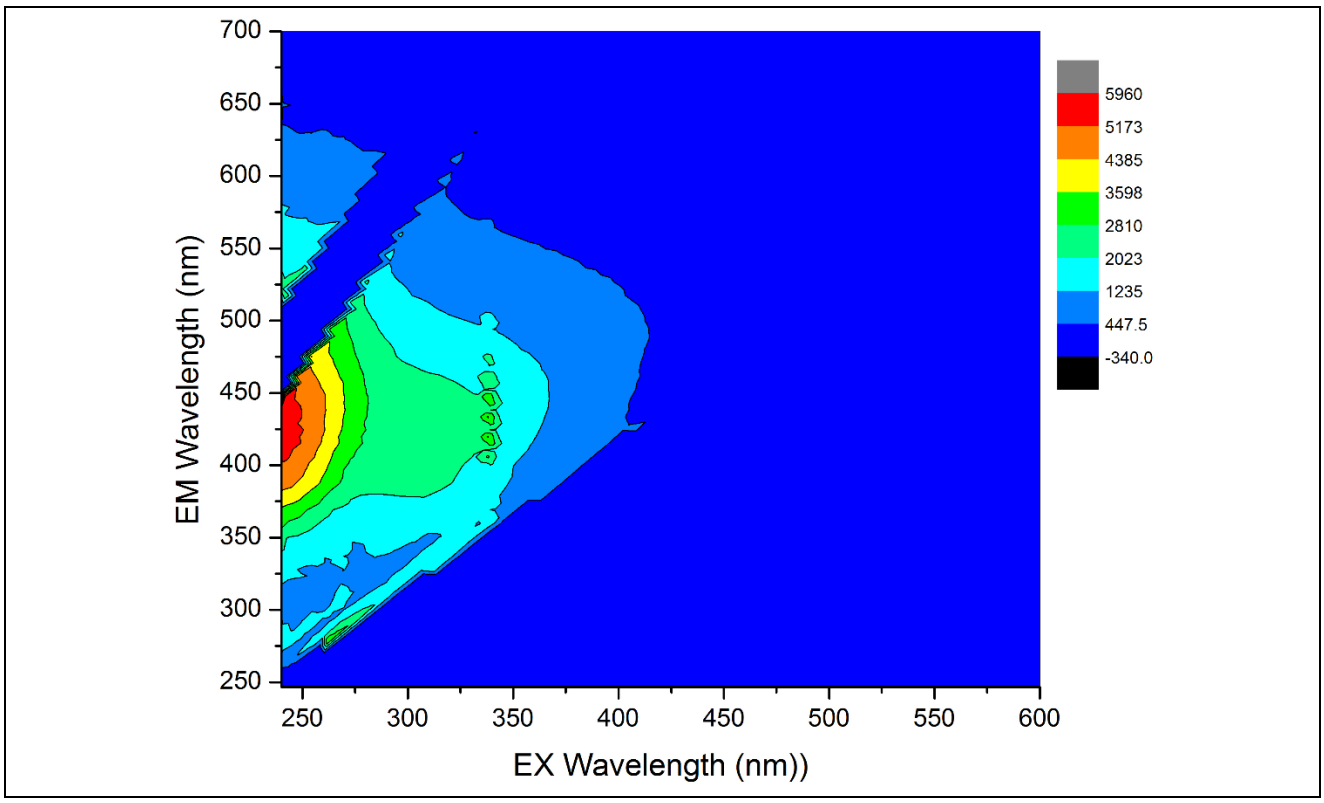


Figure 6-37: FEEM of the source water HPI fraction on day 7 of the THMFP test

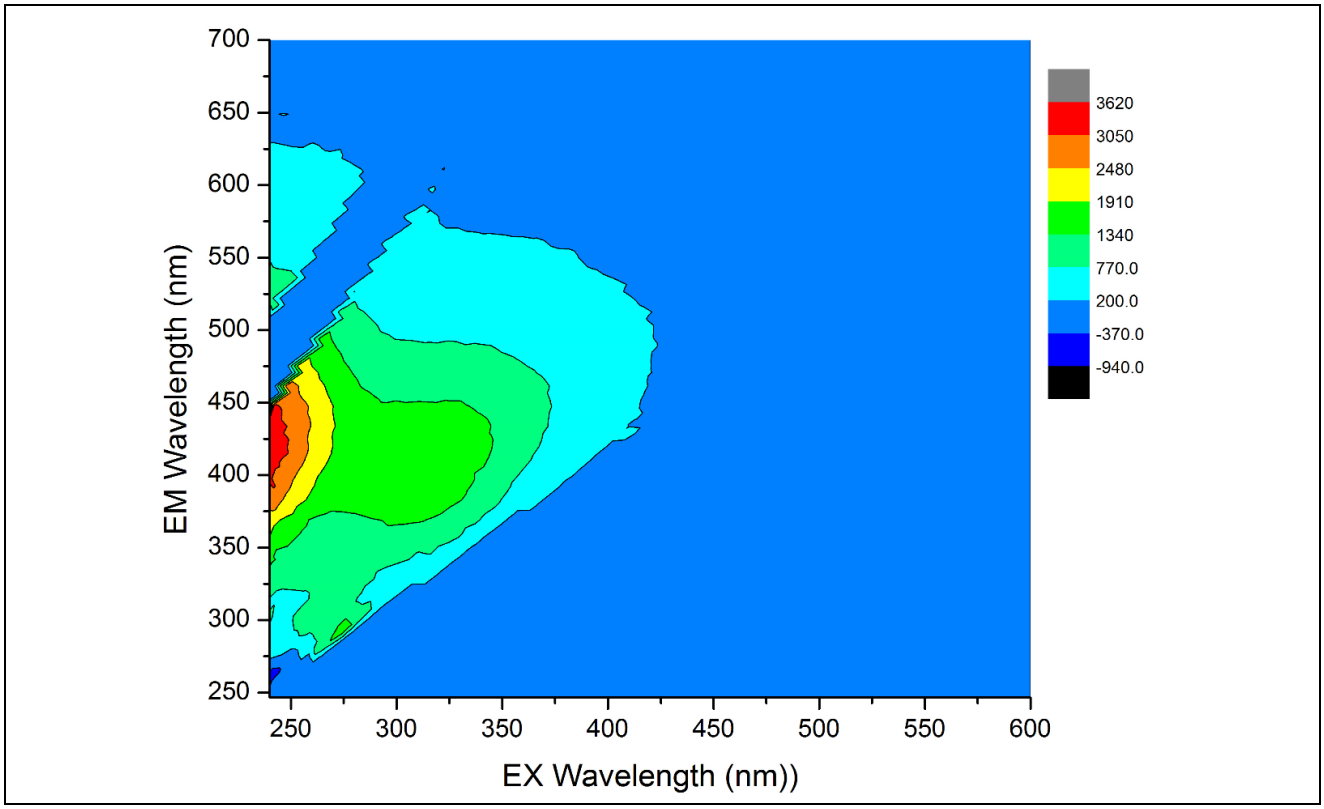


Figure 6-38: FEEM of the source water TPI fraction before THMFP test

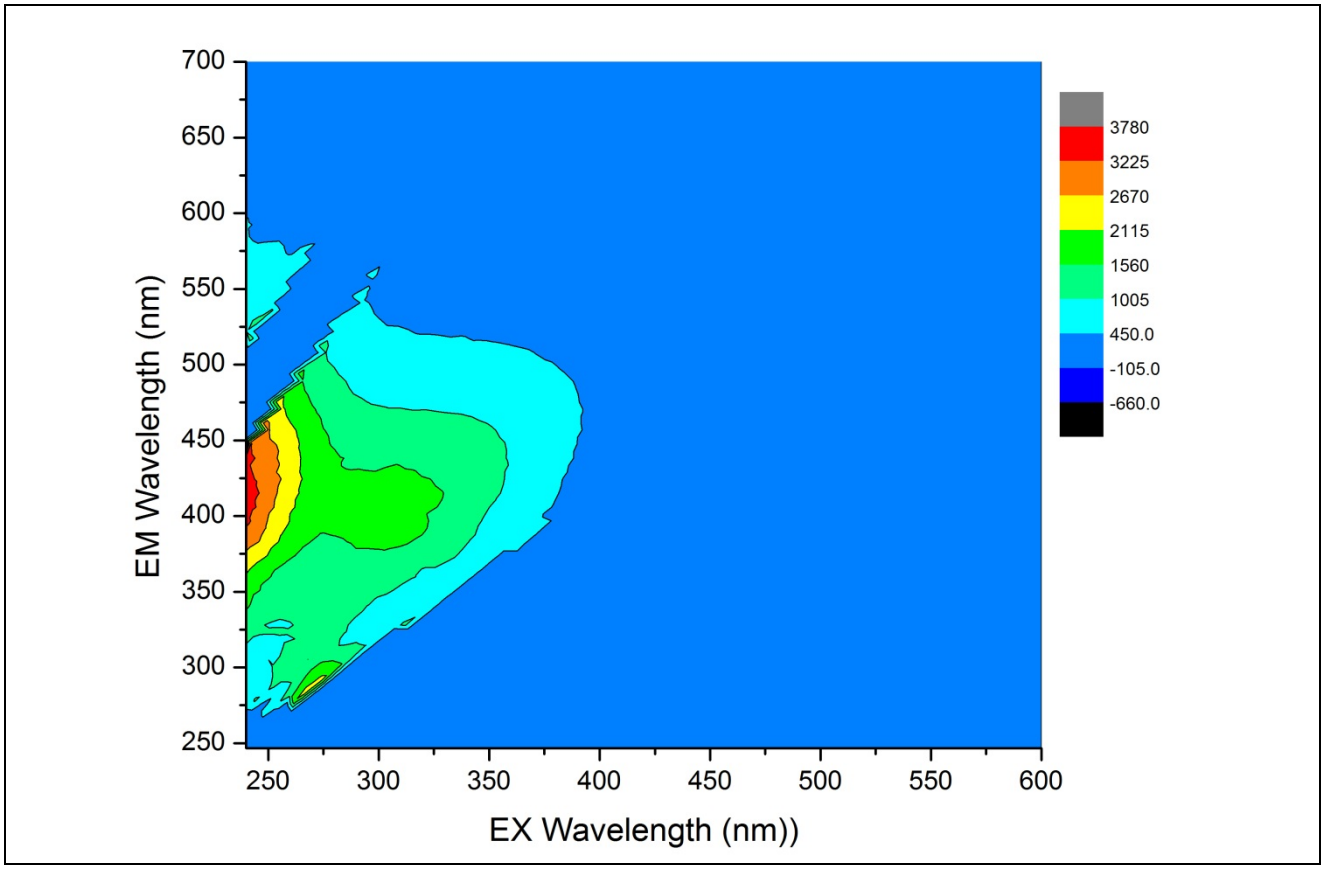


Figure 6-39: FEEM of the source water TPI fraction on day 7 of the THMFP test

6.4 CONCLUSIONS

Although the conventional water treatment processes are capable of removing the HPO NOM fraction, complete removal of this fraction was not achieved. As far as the NOM characterization protocol (PRAM fractionation followed by THMFP and FEEM analyses) is concerned, HPO organic matter holds the highest predisposition to form THMs during chlorination. According to m-PRAM fractionation and the THMFP results, the largest THMFP was observed in the HPO fraction, followed by the TPI and HPI NOM fractions. The successfully enhanced BDOC method performed on the fractioned NOM also identified the HPO NOM of having the highest biodegradability. This suggests that the HPO organic matter is more likely to be mineralised by the bacteria in the water distribution system when compared with the HPI and TPI NOM fractions. The simultaneous determination of THMFP and FEEM interrogated the change in the fluorescence intensity in each fraction during chlorination. Fluorescence regional intergration (FRI) confirmed that the type of organic matter in the Vaal Dam source water is humic-like NOM and this fraction decreased after after chlorination as seen by a decrease in the fluorescence intensity in this region (Region V).

Application of m-PRAM-THMFP-FEEM characterization during full scale drinking water treatment

The m-PRAM technique when utilised in a full scale water treatment plant can be useful in determining the performance of the water treatment process for the removal of the specific NOM fractions. PRAM characterizes NOM based on polarity (HPO, HPI and TPI) and both the parallel and series PRAM technique successfully quantifies the percentage of each NOM fraction removed during the water treatment process.

The PRAM fractionation can be used as a free standing characterization tool or in combination with other NOM characterization techniques to improve the qualitative characterization and removal of the organic matter fraction in question. The added benefit of PRAM fractionation that can be derived by WTP personnel is the identification and removal of a specific fraction of target.

This chapter affirmed the benefit of using advanced NOM characterization technique(s) during full scale drinking water treatment assessing specific NOM fractions removed and identified the fraction more prone to form THMs when using Vaal Dam surface water as source water. Furthermore, the problematic NOM fraction that has the highest BDOC was also identified. The added advantage of being familiar with these characterization techniques and targeting which fraction the treatment plant should focus on in terms of enhanced removal, is of utmost importance when different treatment regimes or alternative water treatment technologies are investigated. This additional knowledge of water treatment performance in terms of specific organic matter fractions removed as well as the method development of an improved 4-day BDOC analysis would be beneficial to the drinking water treatment industry and related stakeholders.

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CHAPTER 7: CONCLUSION AND PERSPECTIVES

The primary aim of this research study was to ascertain NOM treatability at Rand Water, the largest bulk water utility in South Africa. Such an aim was achieved by making use of advanced and rapid NOM characterization techniques, which sought to enable a protocol for the monitoring and treatability of NOM to be proposed. The main findings emanating from this study are that the NOM character of the source water of the utility has now been established and results thereof were published in peer reviewed journals. It is envisaged that the South African water boards and the potable water treatment industry as a whole will benefit from the NOM characterization protocol being proposed in this study. In summary, the proposed protocol involved an initial isolation of the individual NOM fractions followed by the characterization of the NOM fractions using an enhanced-BDOC technique, and the establishment of the THMFP while performing FEEM analysis of the isolated fractions.

It is expected that the isolation of the major NOM fractions followed by an investigation of the effect of these individual NOM fractions on THM formation occurring following the disinfection step could result in the development of a process that is targeted towards the effective removal of NOM during potable water treatment. The development of such a process could be achieved by directing and selecting a specific water treatment technology for the removal of specific problematic NOM fractions. The proposed protocol, which utilises a series of advanced and modified NOM characterization techniques, is envisioned to:

i) Establish the treatability of NOM by determining the removal of the individual NOM fractions during full scale treatment;

ii) Determine the individual NOM fraction that is more prone to THM formation following disinfection with chlorine; and

iii) Identify the fraction that is predisposed to the formation of bacterial regrowth within the distribution system using the newly improved BDOC technique.

This new protocol (m-PRAM fractionation followed by enhanced-BDOC, THMFP and FEEM analyses) was applied at the Rand Water full scale conventional water treatment plant utilising source water from the Vaal Dam.

The major findings of this work, which are presented below, related to the objectives of the study outlined and the research questions posed in **Chapter 1**.

- **Seasonal NOM quantity and quality** – the overall conclusion of the seasonal organic loading is that while the source water DOC increased during the rainy summer months (high flow seasons), a decrease in the corresponding aromaticity (SUVA) led to an increase in the formation of TTHM during the same period. Reduced UV_{254} removal percentages were observed during episodes of low source water SUVA values (< 4 L/mg.m), which often occur during high flow seasons.
- **Effect of seasonal changes on NOM removal** – the removal of NOM was not exclusively affected by a change in seasons (specifically rainfall and temperature patterns). If anything, the role played by the bulk organic loading was much more prominent in relation to the removal of NOM, since periods of increased UV_{254} or DOC values enhances the removal of organic matter. Therefore, it can be concluded that the SUVA values can be relied upon for the prediction of the removal of aromatic NOM by the full scale WTP; high SUVA values (> 5 L/mg.m) generally result in a NOM removal efficiency of between 60 to 80%.
- **Identifying the problematic NOM fraction** – although the full scale conventional water treatment process is generally favourable towards the removal of the HPO NOM fraction, the complete removal of this fraction was however not evident. A significant correlation between the HMW NOM fraction and THM formation was observed when the molecular size distribution of NOM was analysed; this seems to indicate that chloroform formation is largely influenced by HMW NOM of the Vaal Dam surface water.
- **Effect of NOM polarity (m-PRAM) on DBP formation** – when used as a free standing characterization tool the modified-PRAM technique was used for the effective treatability assessment of NOM. In this study, the m-PRAM was nonetheless combined with other NOM characterization tools such as BDOC, FEEM and THMFP. Resulting from PRAM fractionation the HPO component constituted 35% of the organic matter and had the highest THMFP (39.1%), compared to the HPI and TPI fractions. These results suggest that the HPO NOM component of this oligotrophic water source has a high propensity to form THMs.
- **Enhanced-BDOC technique** – one of the major achievements of this study was the improvement and successful application of the enhanced-BDOC technique, for

illustrating that the HPO NOM fraction possesses a high biodegradability. The HPO NOM fraction, which promotes the formation of bacterial re-growth in the drinking water distribution system, is therefore more likely to be degraded by heterotrophic bacteria prevailing in the distribution sytem.

- **THMFP and FEEM assessments of humic acid-like material** - the simultaneous determination of THMFP and FEEM enabled an assessment of the change in the fluorescence intensity within each NOM fraction during chlorination. Fluorescence regional integration (FRI) indicated that the humic acid-like material (Region V) of the HPO fraction was more likely to react with chlorine and a precursor to THM formation.
- **NOM characterization and monitoring protocol** - the NOM fraction that is not effectively removed by the water treatment process, easily biodegraded by heterotrophic bacteria and the fraction that is more likely to form THMs was identified by utilising the proposed protocol (m-PRAM, e-BDOC, THMFP and FEEM).

Although the set research aims and objectives of this project have been achieved, it is recommended that further research be undertaken at Rand Water to address the issues raised in this work. In this regard, the specific research that can be undertaken is as follows:

- **Validating the NOM characterization and monitoring protocol** on different source waters and investigating the frequency of the monitoring programme.
- **Haloacetic acid formation potential (HAAFP) of NOM fractions** - since the THMFP of the individual fractions within Vaal Dam source water has now been determined with the HPO fraction having the highest propensity to form THMs, the haloacetic acid formation potential (HAAFP) of the individual fractions should also be investigated.
- **Combination of enhanced-BDOC method and FEEM** - further research on the developed enhanced-BDOC method can incorporate the concurrent analysis of FEEM during the 4-day BDOC method, in order to establish the change in fluorescence intensity during bacterial degradation of the isolated NOM fractions.
- **Quantitative analysis of heterotrophic bacterial communities using flow cytometry** - lastly, an investigation on the use of flow cytometry as a growth enumeration technique for the quantitative determination of heterotrophic bacterial communities during the 4-day BDOC method on the isolated HPO, HPI and TPI NOM fractions is also recommended.

APPENDIX

APPENDIX A: CHARACTERIZATION RESULTS

Table A-1: UV_{254} during THMFP study

		Day 0 (m^{-1})	Day 1 (m^{-1})	Day 2 (m^{-1})	Day 3 (m^{-1})	Day 4 (m^{-1})	Day 5 (m^{-1})	Day 6 (m^{-1})	Day 7 (m^{-1})
Bulk (unfractioned)									
Source water	21.1	12.6	10.6	12.9	18.2	12.3	13.3	12.2	18.2
Treated water	10.8	7.3	6.9	7.1	8.3	6.1	6.3	6.9	7.8
HPO									
Soure water	23.4	17.1	16.6	15.4	19.2	14.0	16.7	15.0	19.6
Treated water	12.0	9.2	7.9	8.1	10.3	6.9	8.0	8.7	9.3
HPI									
Soure water	20.3	13.9	14.1	13.9	16.9	11.8	11.5	12.3	16.1
Treated water	10.6	7.1	7.0	7.0	8.2	6.1	6.7	6.6	7.9
TPI									
Soure water	12.4	9.5	9.5	13.5	13.4	13.3	12.5	10.8	13.5
Treated water	7.5	8.8	8.4	11.6	7.4	10.8	9.2	9.0	7.8

Table A-2: Peak heights of the source water obtained from HPSEC

Date	Peak I (mAU)	Peak II (mAU)	Peak III (mAU)	Peak IV (mAU)	Peak V (mAU)	Peak VI (mAU)
17-Jul	13.008	17.418	18.967	16.708	11.405	3.817
24-Jul	13.173	17.409	18.917	16.654	11.438	3.776
31-Jul	13.174	17.500	19.135	17.002	11.862	5.322
13-Aug	11.949	16.888	18.891	16.927	11.307	3.288
20-Aug	12.873	17.031	18.498	16.326	11.144	4.030
27-Aug	13.111	17.125	18.655	16.667	11.487	3.717
3-Sep	10.667	15.593	17.647	15.843	10.774	4.855
17-Sep	12.149	16.430	18.077	16.093	10.792	3.770
25-Sep	11.907	16.259	17.894	15.909	10.843	3.994
22-Oct	11.056	15.248	17.057	15.359	10.658	4.846
5-Nov	9.814	14.434	16.555	14.825	10.185	3.588
12-Nov	9.748	14.295	16.360	14.593	10.009	3.057
19-Nov	9.459	14.139	16.275	14.746	10.352	3.173
26-Nov	10.706	13.678	15.602	14.725	10.182	2.758
4-Dec	9.202	13.832	16.011	14.493	10.115	3.232
10-Dec	8.785	13.392	15.557	14.104	9.741	3.004
14-Jan	8.247	12.671	14.739	13.390	9.449	3.184
20-Jan	7.931	12.302	14.393	13.195	9.331	3.124
4-Feb	7.919	12.085	14.024	12.852	9.282	3.026
11-Feb	7.142	11.568	16.011	14.493	10.115	3.060
18-Feb	7.060	11.085	13.144	12.190	8.730	2.992

Table A-3: Percentage DOC recovery during m-PRAM of source water

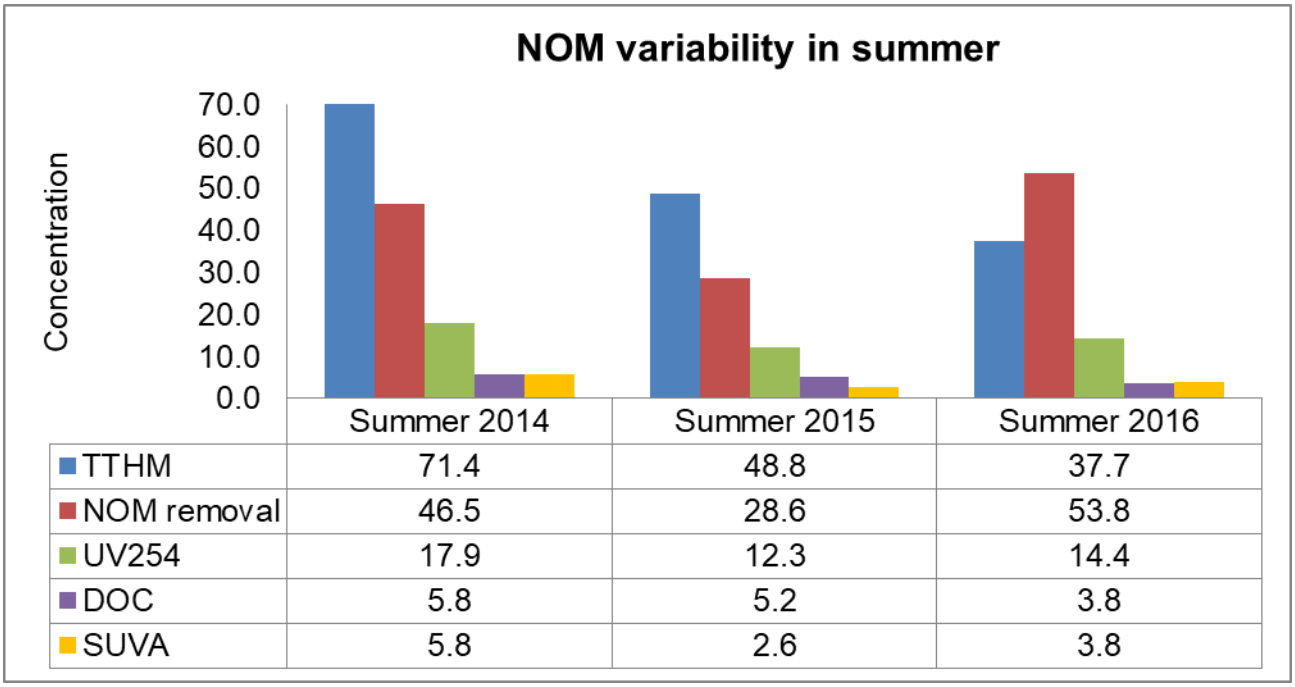
Fraction	DOC (mg/L)	Sample vol (L)	DOC mass (mg)
Sample A			
Unfractioned	4.9	2.0	9.8
HPO	7.5	0.3	2.3
HPI	5.0	0.3	1.5
TPI	11.0	0.5	5.5
Total DOC mass			9.3
Recovered (%)			**94.4**
Sample B			
Unfractioned	4.6	2.0	9.2
HPO	6.2	0.3	1.9
HPI	4.8	0.3	1.4
TPI	11.0	0.5	5.5
Total DOC mass			8.8
Recovered (%)			**95.7**
Sample C			
Unfractioned	4.0	2.0	8.0
HPO	3.8	0.3	1.1
HPI	3.5	0.3	1.1
TPI	11.0	0.5	5.5
Total DOC mass			7.7
Recovered (%)			**96.1**
Sample D			
Unfractioned	3.9	2.0	7.8
HPO	9.8	0.3	2.9
HPI	6.7	0.3	2.0
TPI	4.7	0.5	2.4
Total DOC mass			7.3
Recovered (%)			**93.6**
Sample E			
Unfractioned	4.7	2.0	9.4
HPO	5.8	0.3	1.7
HPI	4.7	0.3	1.4
TPI	9.5	0.5	4.8
Total DOC mass			7.9
Recovered (%)			**93.8**

Table A-4: UV_{254}, DOC and SUVA in Vaal Dam surface water

2015				2016			
Month	UV_{254} (m^{-1})	DOC (mg/L)	SUVA (L/mg.m)	Month	UV_{254} (m^{-1})	DOC (mg/L)	SUVA (L/mg.m)
14-Jan	18.1	4.2	4.3	6-Jan	7.8	3.9	2.0
28-Jan	11.9	4.4	2.7	20-Jan	18.3	4.7	3.9
11-Feb	11.0	4.2	2.6	3-Feb	16.6	3.1	5.3
25-Feb	10.6	4.7	2.3	17-Feb	6.2	2.8	2.2
11-Mar	10.1	3.9	2.6	2-Mar	19.0	3.9	4.9
1-Apr	9.5	4.4	2.2	16-Mar	17.9	3.1	5.8
15-Apr	12.5	4.3	2.9	6-Apr	20.2	4.0	5.1
29-Apr	10.2	5.0	2.0	20-Apr	13.7	3.4	4.0
13-May	9.6	4.9	2.0	4-May	14.2	4.4	3.2
27-May	10.6	4.4	2.4	18-May	17.8	4.0	4.4
10-Jun	11.2	3.5	3.2	1-Jun	18.9	3.2	5.9
1-Jul	11.1	3.4	3.3	15-Jun	19.6	2.9	6.7
15-Jul	8.9	3.0	3.0	6-Jul	21.6	3.0	7.2
29-Jul	10.8	4.0	2.7	22-Jul	18.9	3.6	5.2
12-Aug	12.2	6.5	1.9	17-Aug	8.7	2.4	3.6
9-Sep	20.3	3.6	5.7	31-Aug	12.5	2.8	4.5
30-Sep	18.7	3.7	5.1	5-Oct	11.4	3.0	3.8
14-Oct	18.1	4.9	3.7	19-Oct	14.0	3.2	4.4
28-Oct	22.7	4.0	5.7	2-Nov	10.3	3.9	2.7
11-Nov	24.1	4.0	6.0	16-Nov	8.4	3.1	2.7
25-Nov	21.7	4.7	4.6	30-Nov	10.2	2.2	4.6
9-Dec	18.7	4.1	4.6	14-Dec	18.5	3.0	6.2

Table A-5: THMFP in the source and full scale treated water fractions

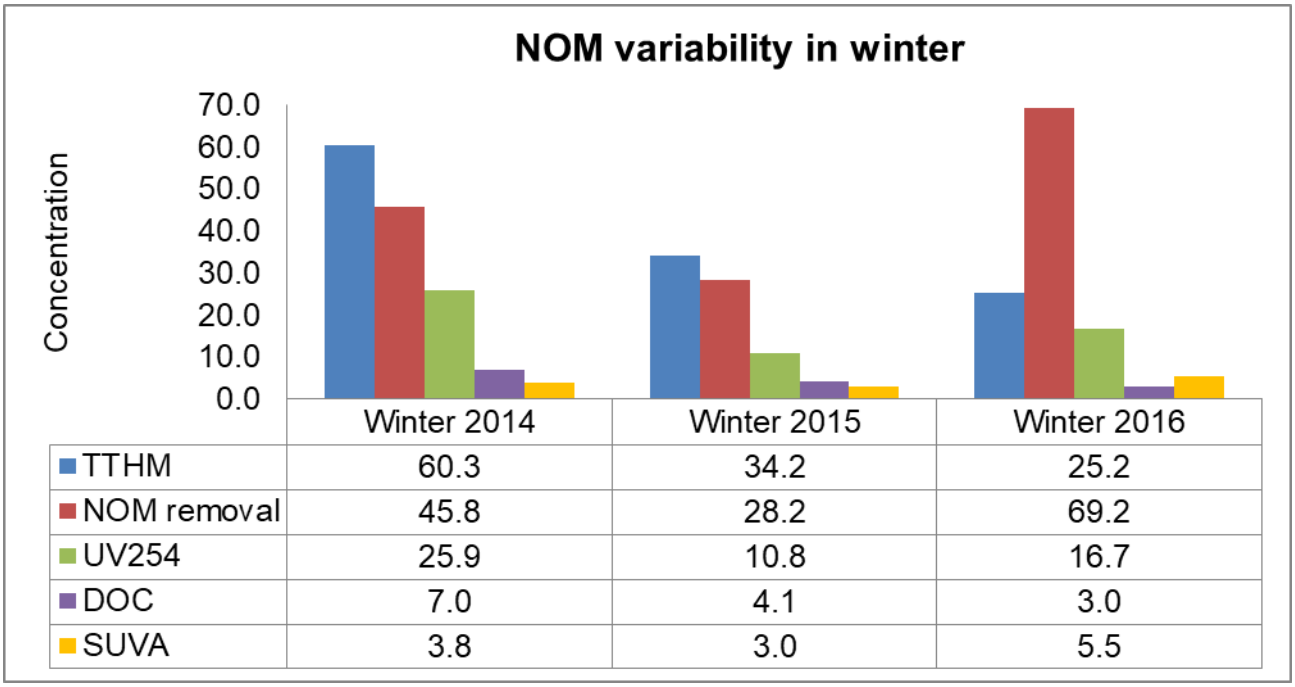
	$TTHM_{final} - TTHM_{initial}$ (µg/L)			
Source water				
HPO	224	189	116	110
HPI	164	139	100	82
TPI	172	146	106	87
Treated water				
HPO	156	116	98	78
HPI	104	65	60	44
TPI	110	65	70	58



	Summer 2014	Summer 2015	Summer 2016
TTHM	71.4	48.8	37.7
NOM removal	46.5	28.6	53.8
UV254	17.9	12.3	14.4
DOC	5.8	5.2	3.8
SUVA	5.8	2.6	3.8

Figure A-1: Average organic loading in the source water in summer, % NOM (UV_{254}) removal after full scale treatment and TTHM (in the full scale treated water)

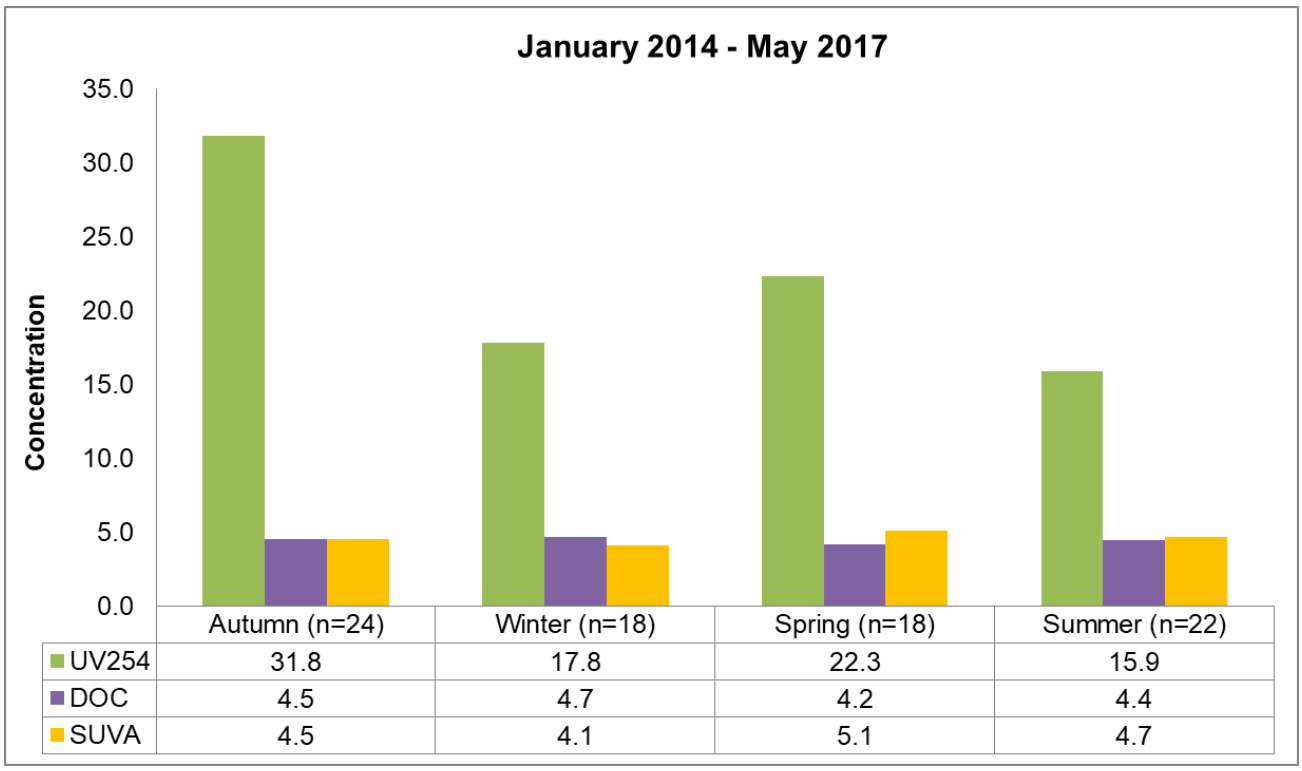
UV_{254} : m^{-1}, DOC : mg/L, SUVA : L/mg.m, TTHM : µg/L



	Winter 2014	Winter 2015	Winter 2016
TTHM	60.3	34.2	25.2
NOM removal	45.8	28.2	69.2
UV254	25.9	10.8	16.7
DOC	7.0	4.1	3.0
SUVA	3.8	3.0	5.5

Figure A-2: Average organic loading in the source water in winter, % NOM (UV_{254}) removal after full scale treatment and TTHM (in the full scale treated water)

UV_{254} : m^{-1}, DOC : mg/L, SUVA : L/mg.m, TTHM : µg/L



	Autumn (n=24)	Winter (n=18)	Spring (n=18)	Summer (n=22)
UV254	31.8	17.8	22.3	15.9
DOC	4.5	4.7	4.2	4.4
SUVA	4.5	4.1	5.1	4.7

Figure A-3: Seasonal organic loading in Vaal Dam surface water

UV_{254} : m^{-1}, DOC : mg/L, SUVA : L/mg.m

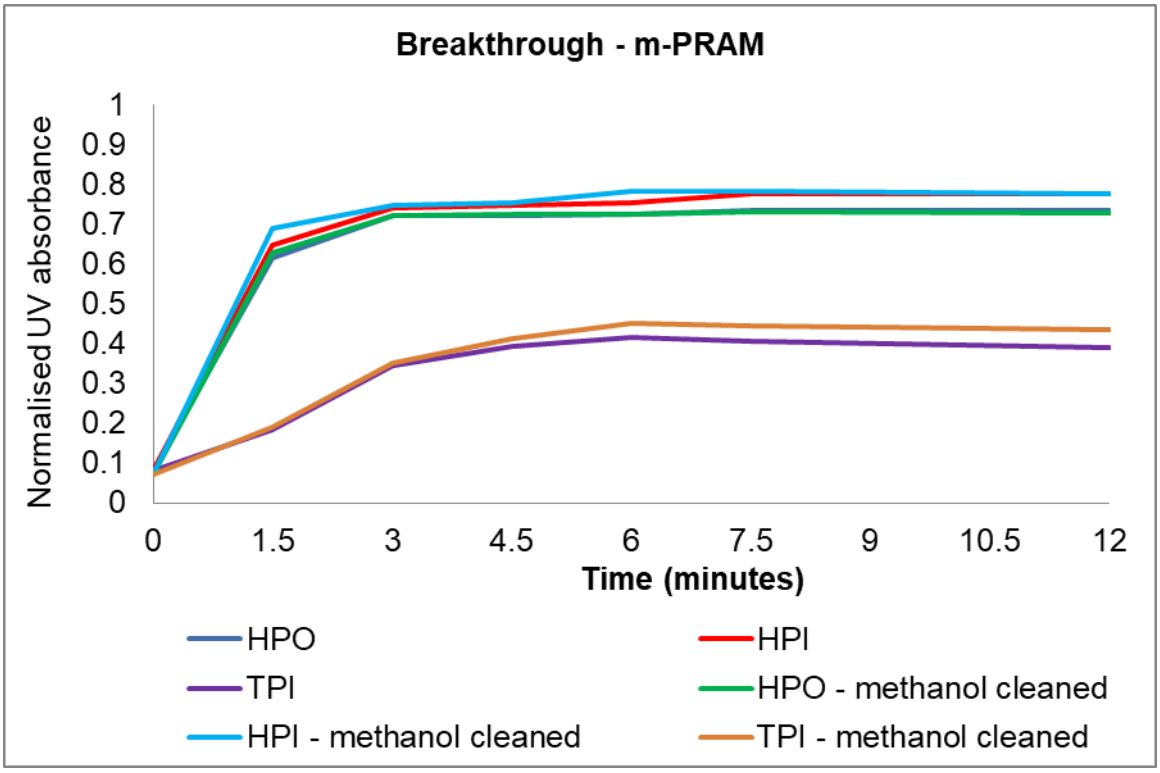


Figure A-4: Comparison of the normalised breakthrough curves obtained from m-PRAM on the source water after cleaning SPE cartridges with methanol

HPO : C18 SPE cartridge, HPI : CN SPE cartridge, TPI : NH_2 SPE cartridge

APPENDIX B: UV_{254} ABSORBANCE DURING THE 7 DAY THMFP INVESTIGATION

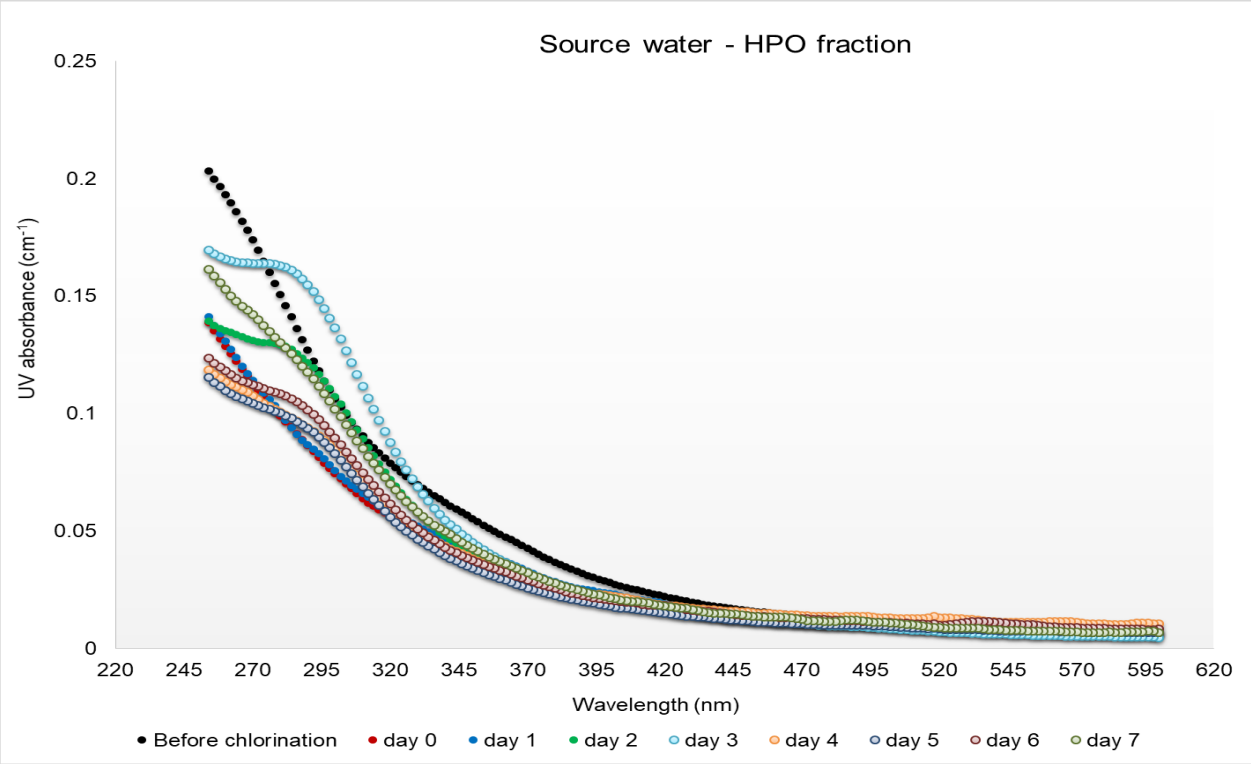


Figure B-1: UV_{254} absorbance spectra of the source water HPO fraction

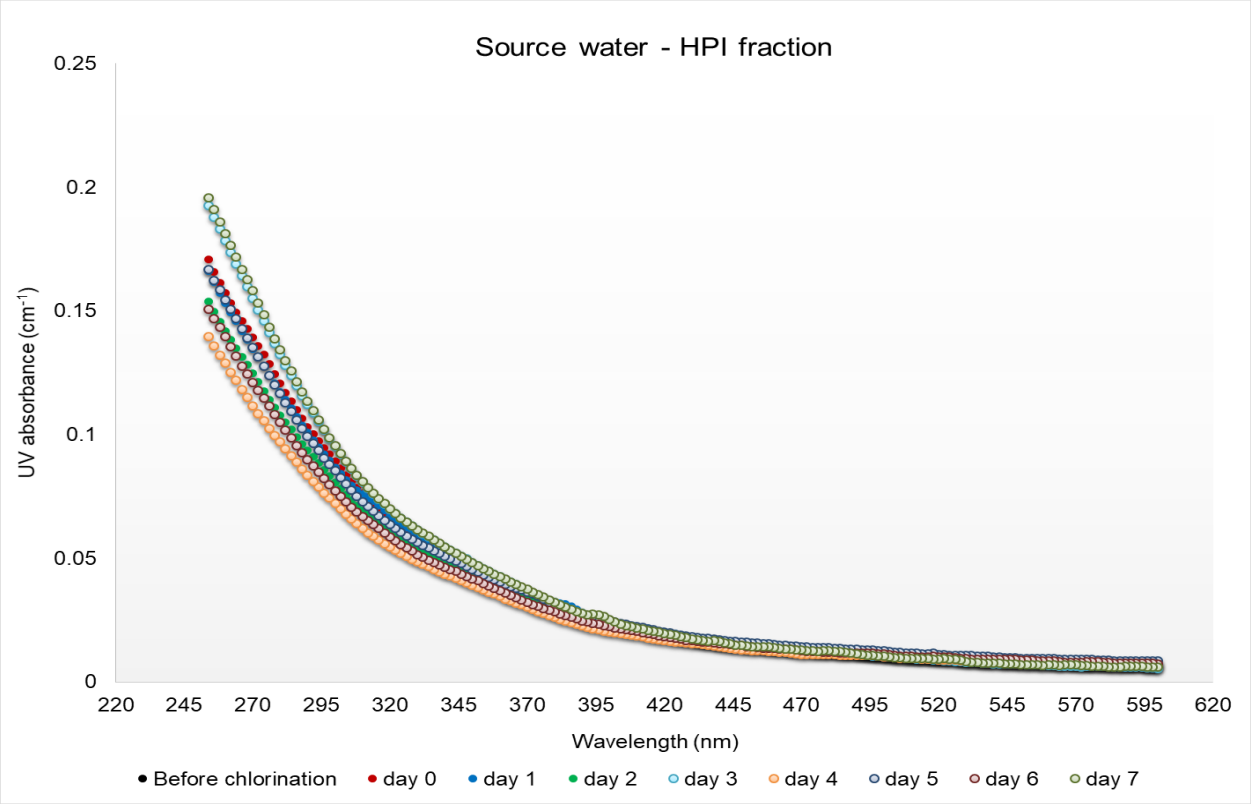


Figure B-2: UV_{254} absorbance spectra of the source water HPI fraction

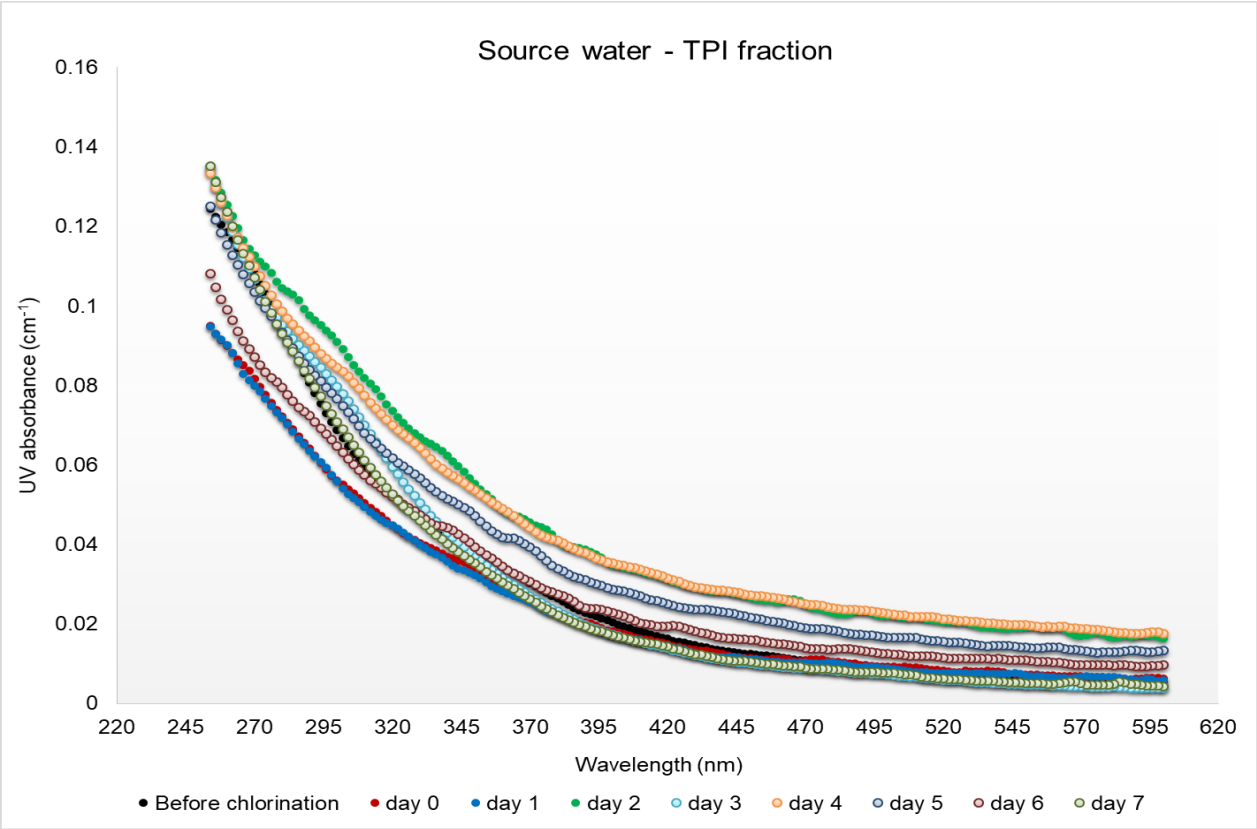


Figure B-3: UV_{254} absorbance spectra of the source water TPI fraction

APPENDIX C: FEEM DURING THE 7 DAY THMFP INVESTIGATION

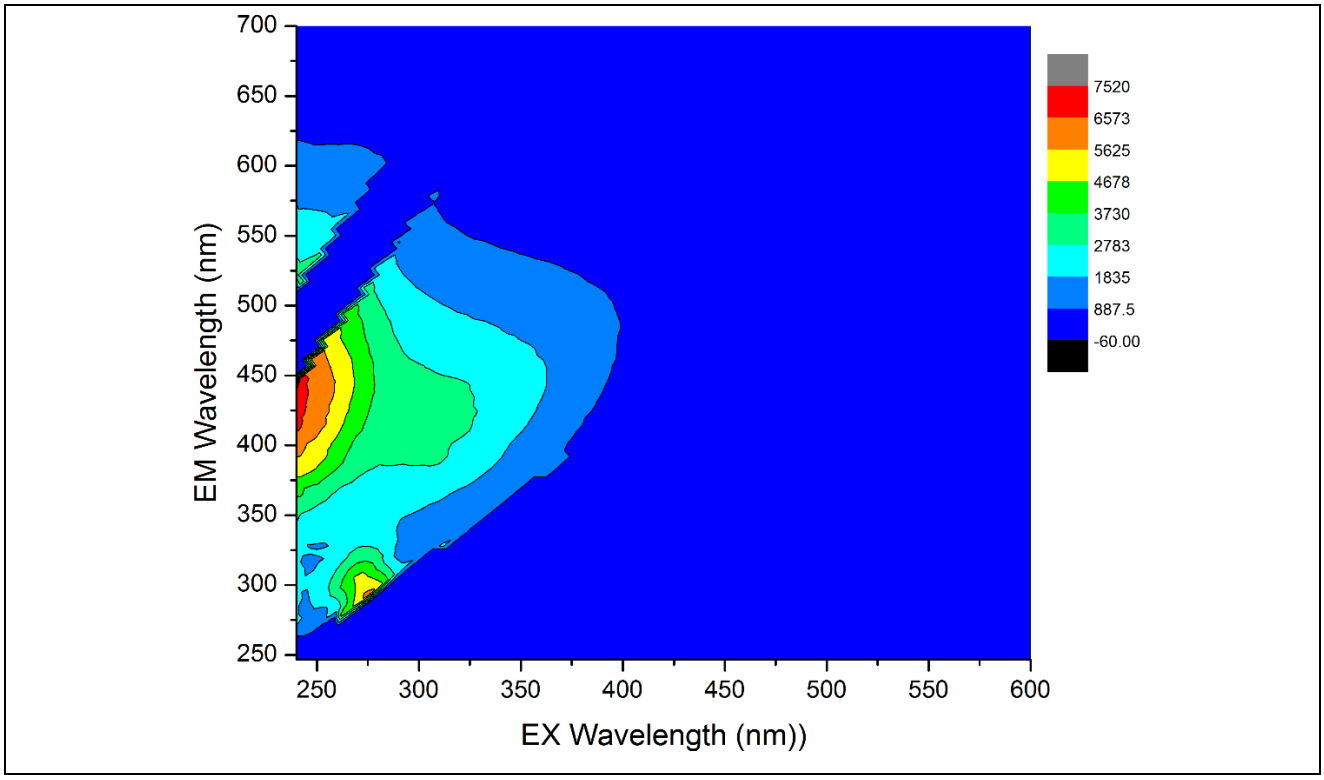


Figure C-1: FEEM on the bulk (unfractioned) source water before THMFP test

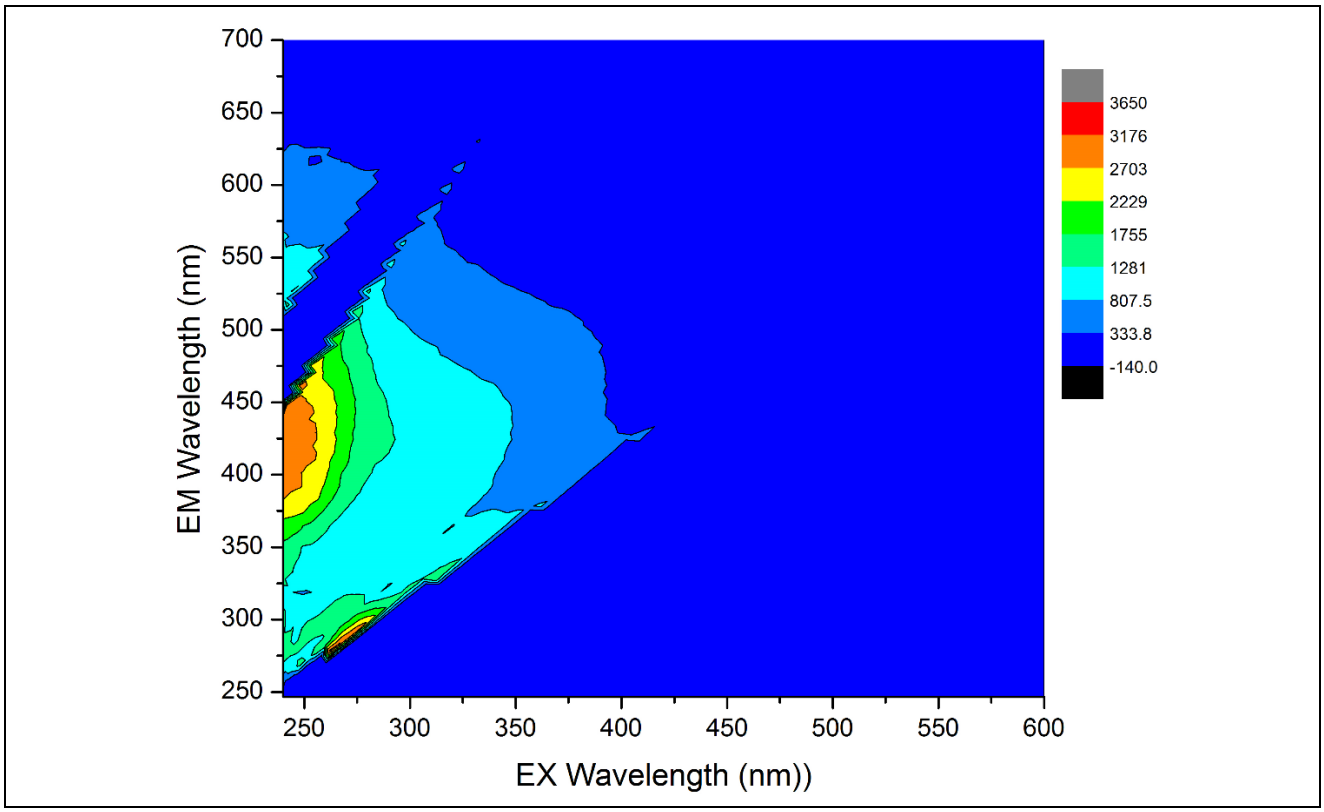


Figure C-2: FEEM on the bulk (unfractioned) source water on day 3 of the THMFP test

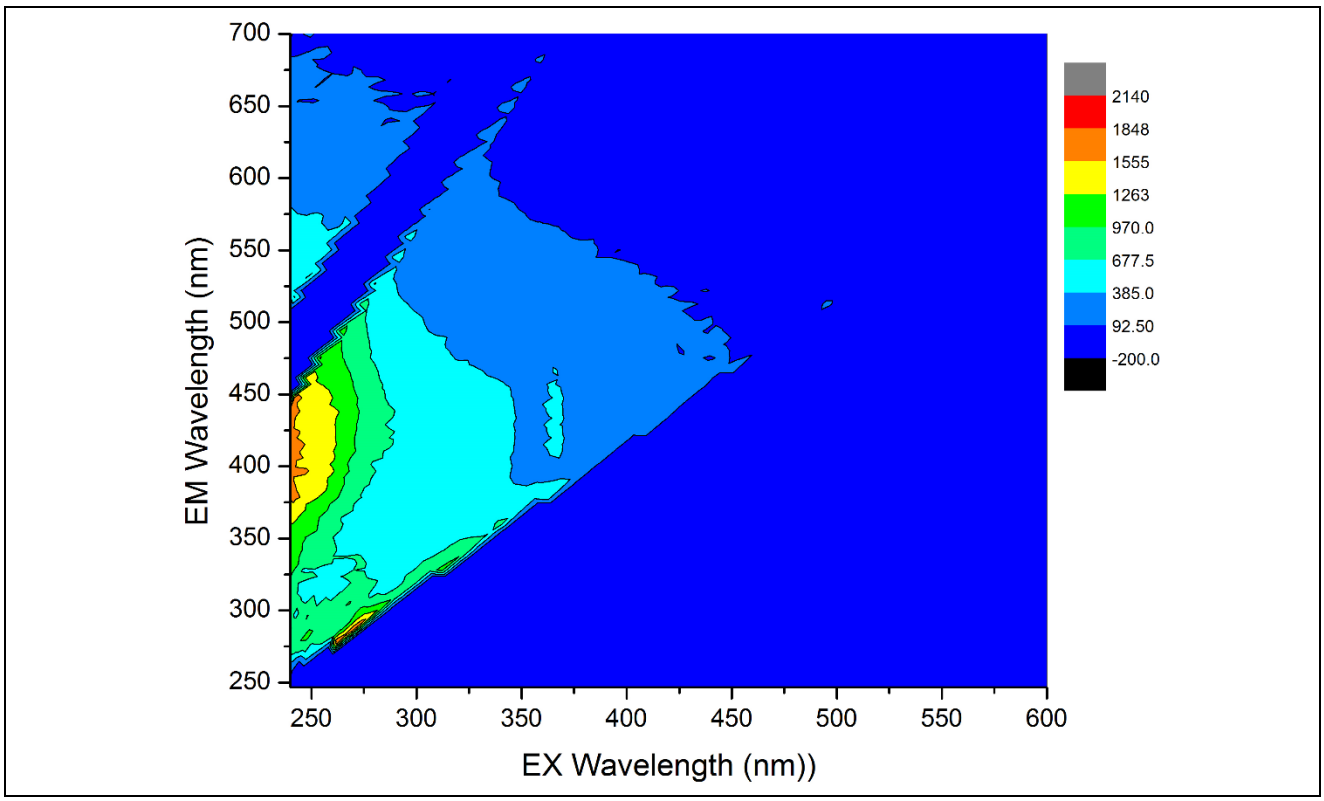


Figure C-3: FEEM on the bulk (unfractioned) source water on day 4 of the THMFP test

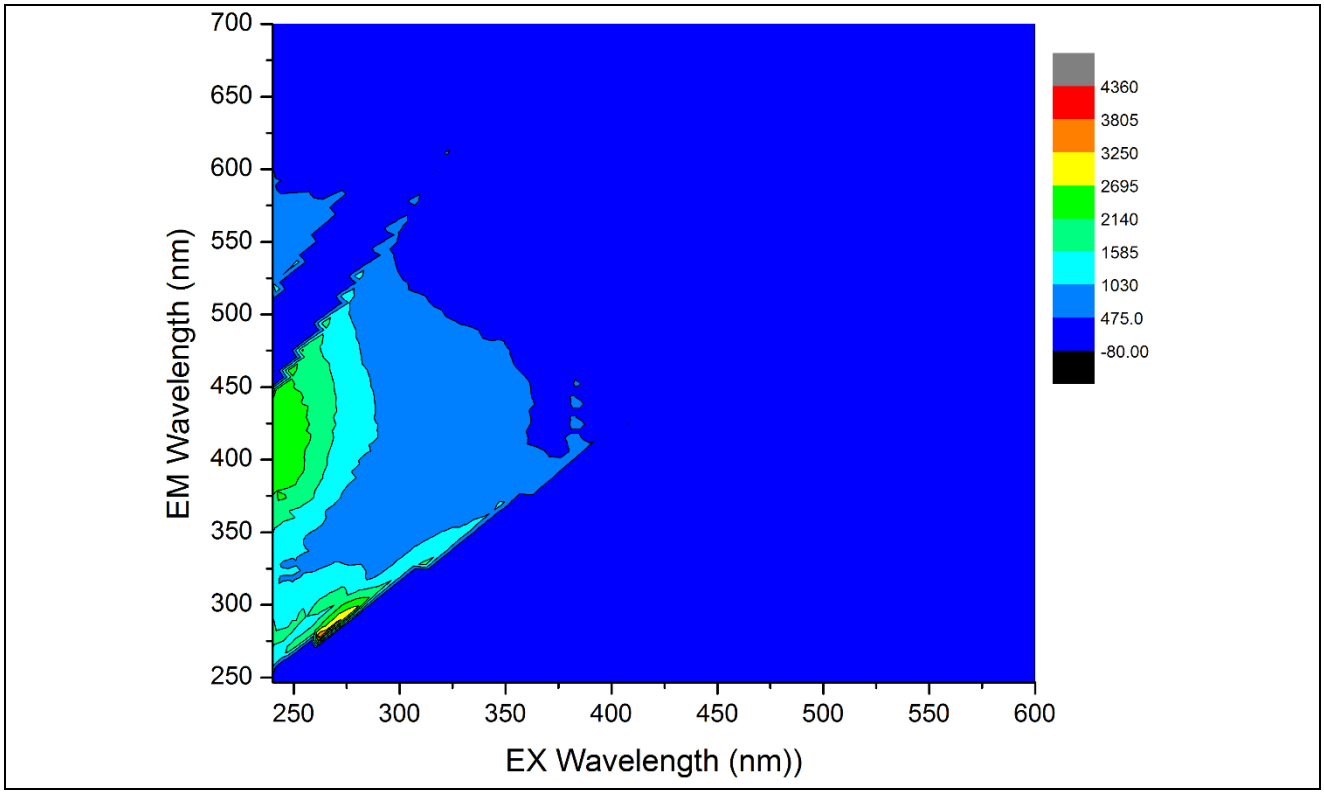


Figure C-4: FEEM on the bulk (unfractioned) source water on day 7 of the THMFP test

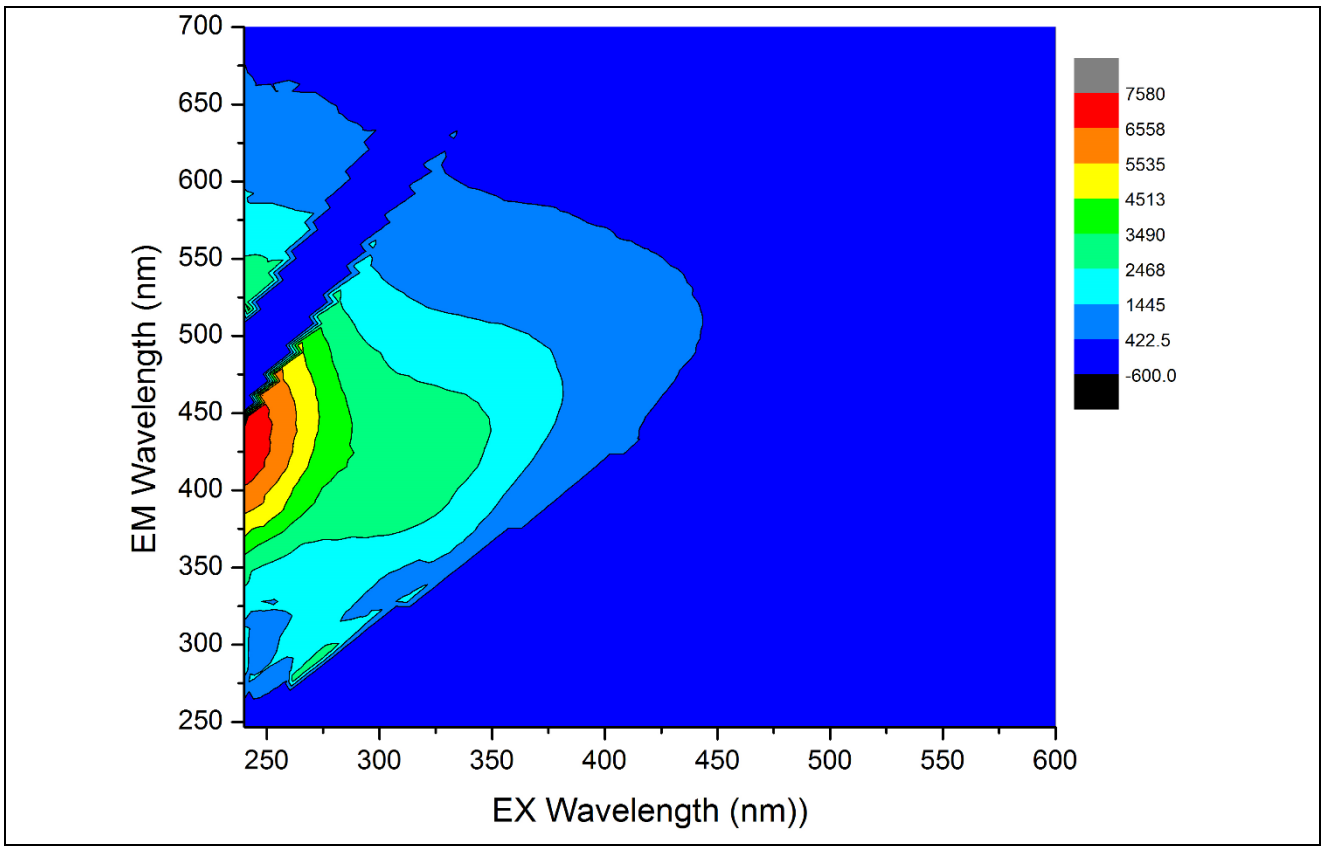


Figure C-5: FEEM on the source water HPO fraction before THMFP test

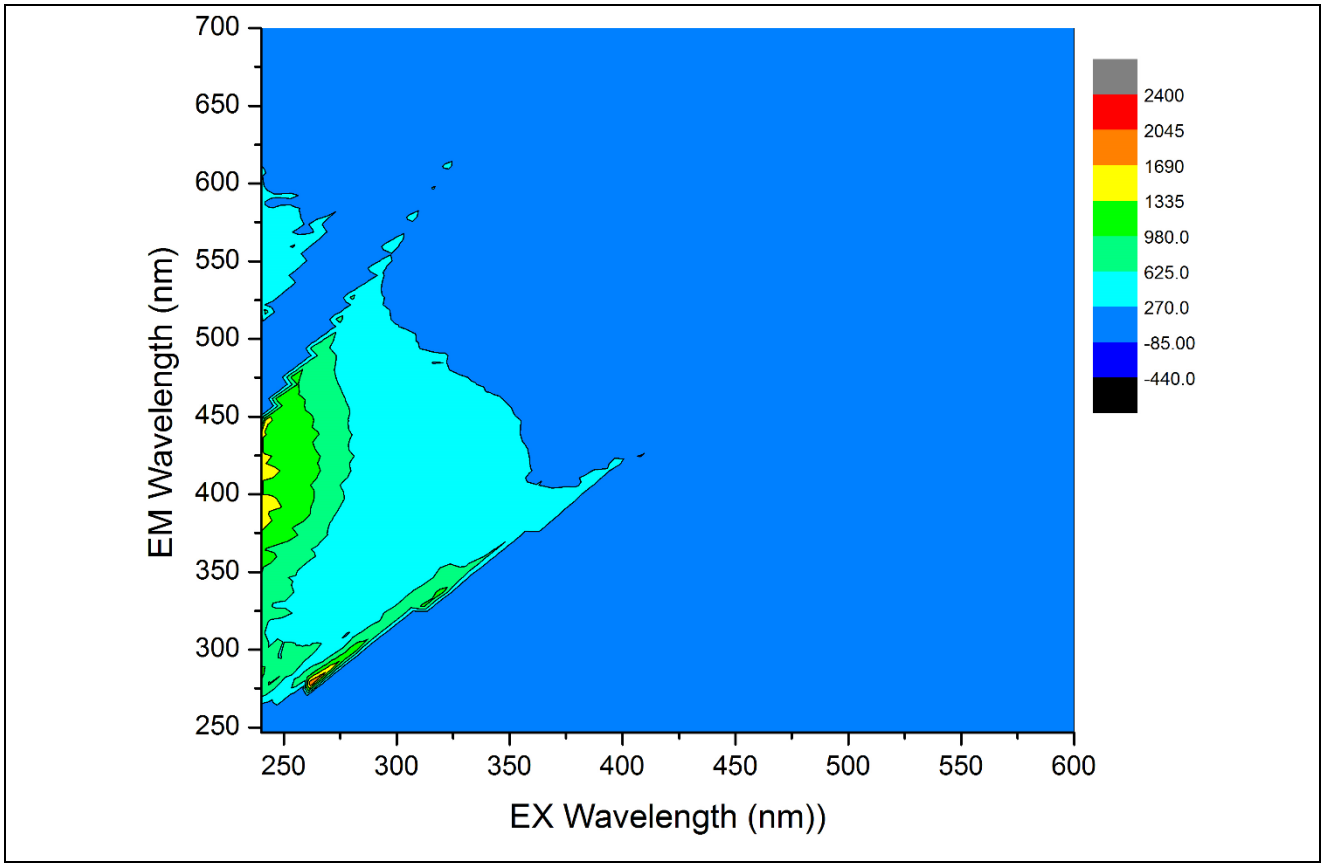


Figure C-6: FEEM on the source water HPO fraction on day 2 of the THMFP tes

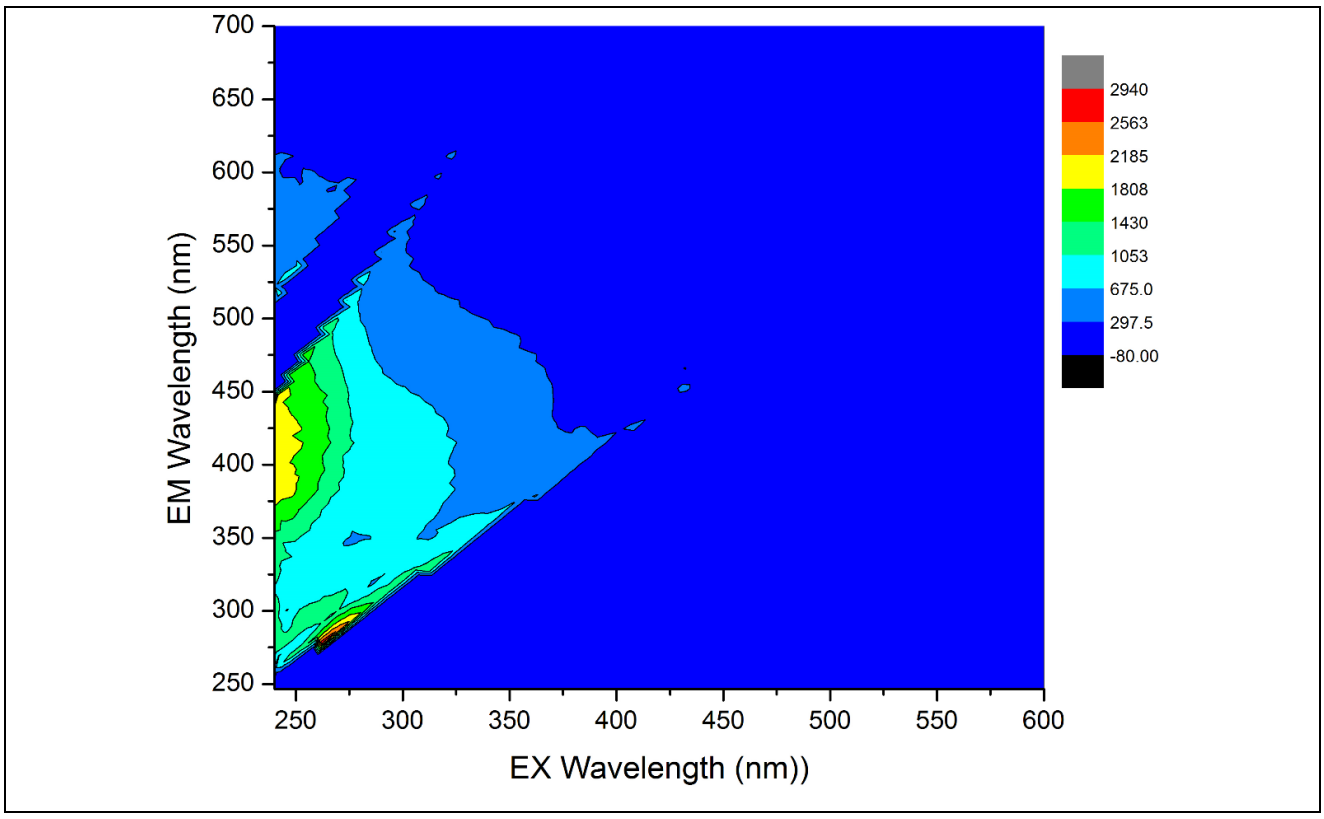


Figure C-7: FEEM on the source water HPO fraction on day 7 of the THMFP test

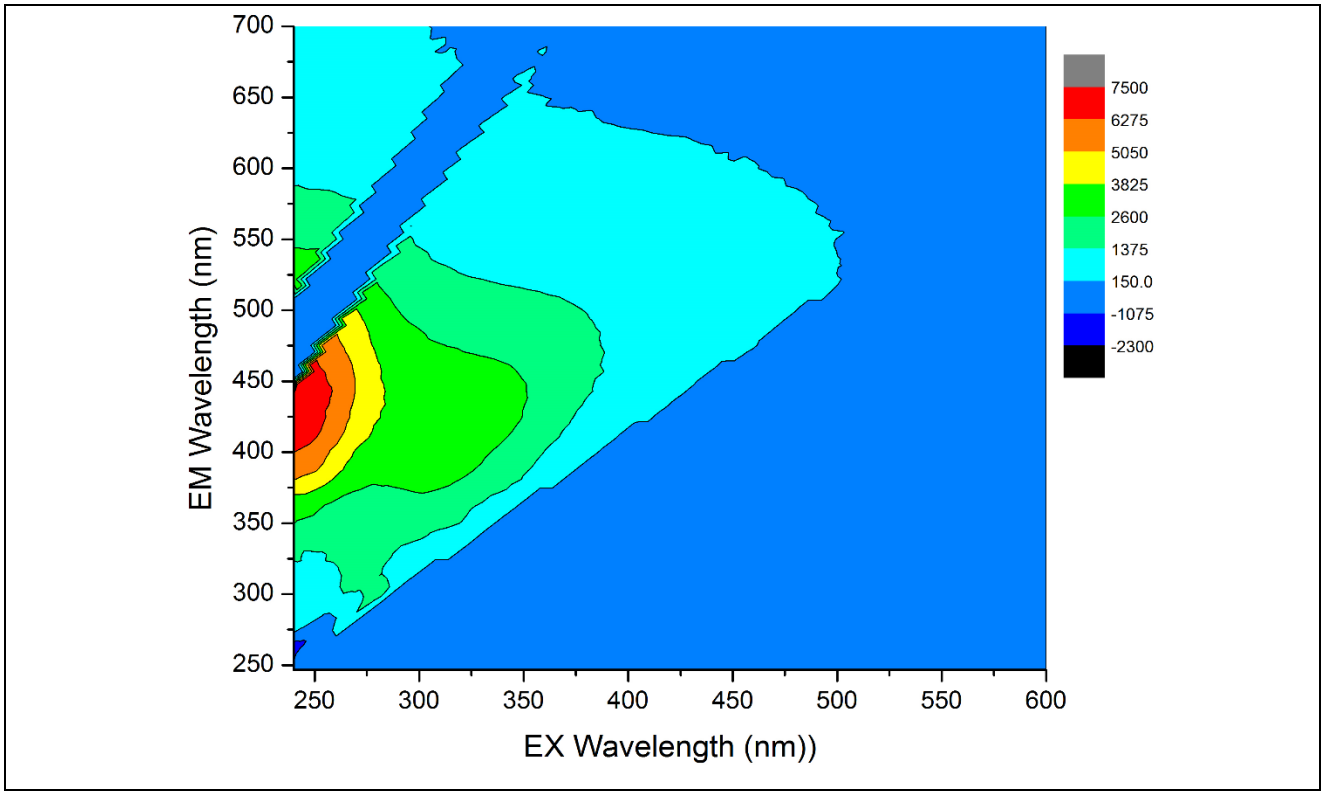


Figure C-8: FEEM on the source water HPI fraction before THMFP test

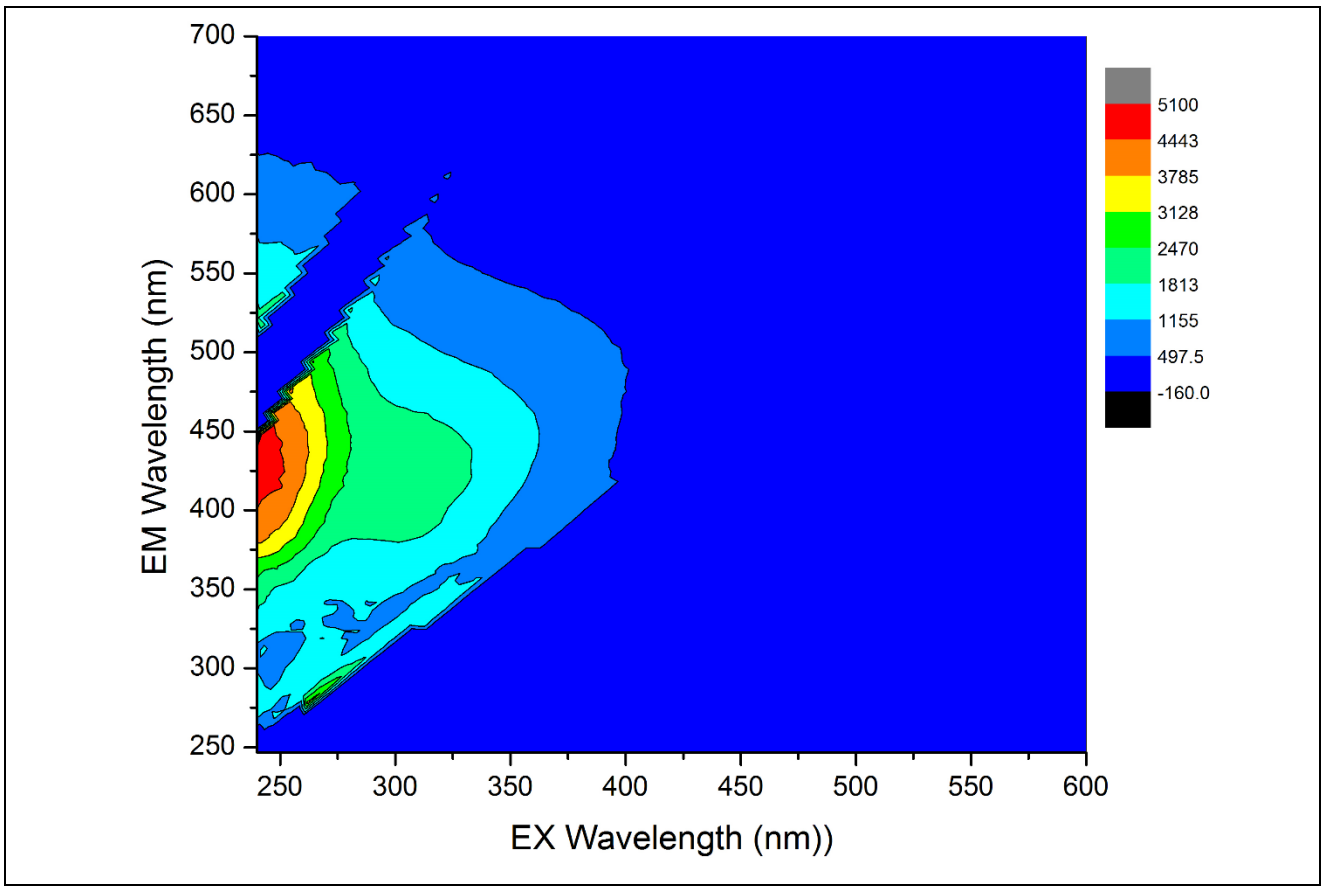


Figure C-9: FEEM on the source water HPI fraction on day 3 of the THMFP test

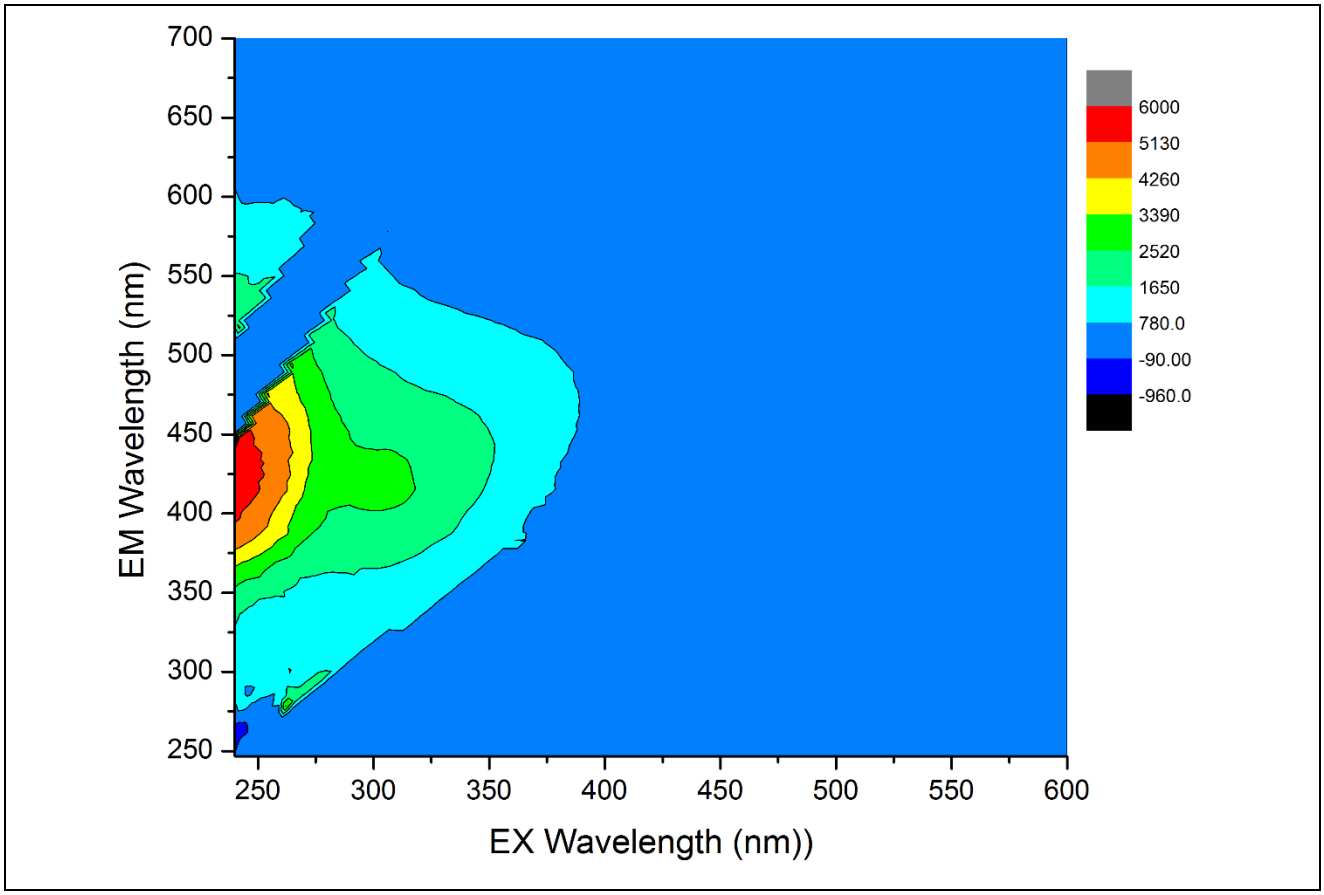


Figure C-10: FEEM on the source water HPI fraction on day 5 of the THMFP test

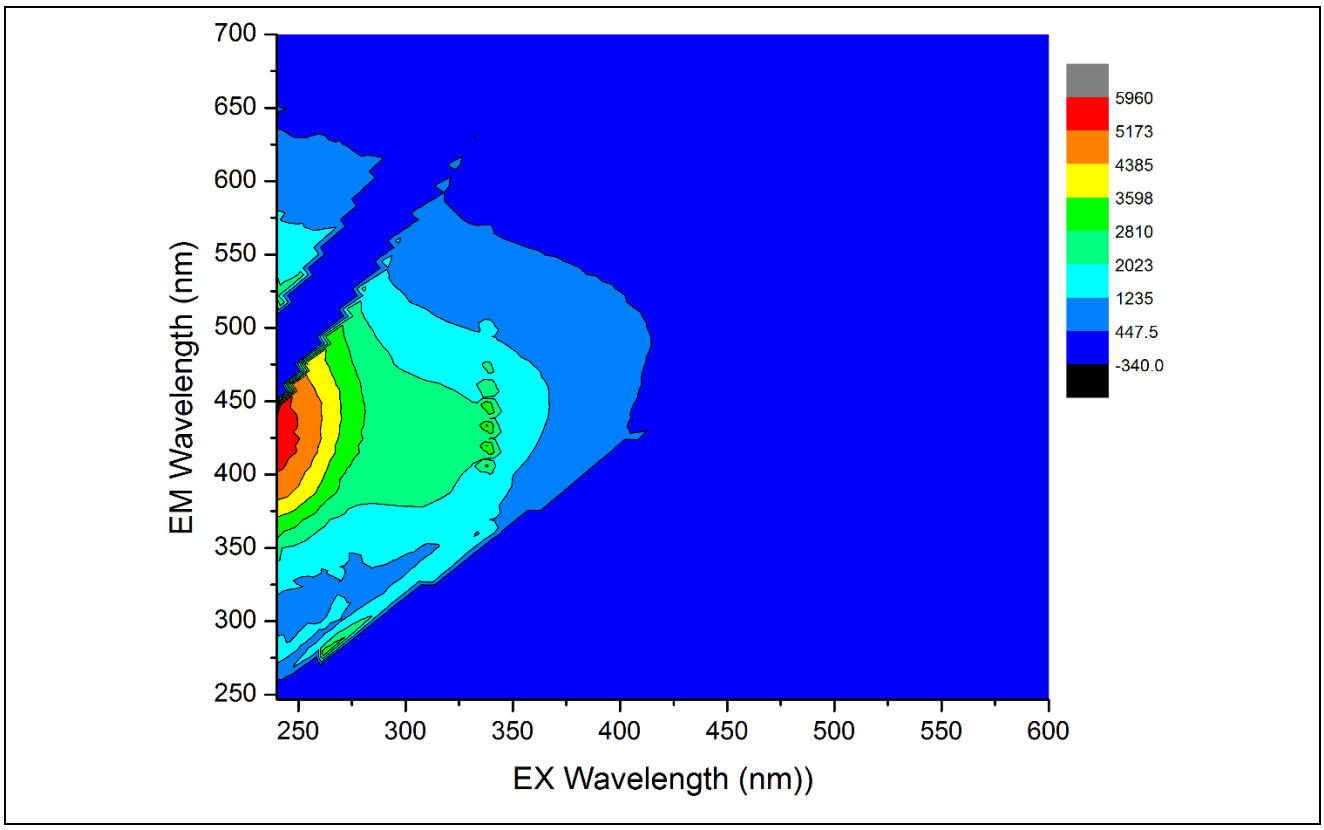


Figure C-11: FEEM on the source water HPI fraction on day 7 of the THMFP test

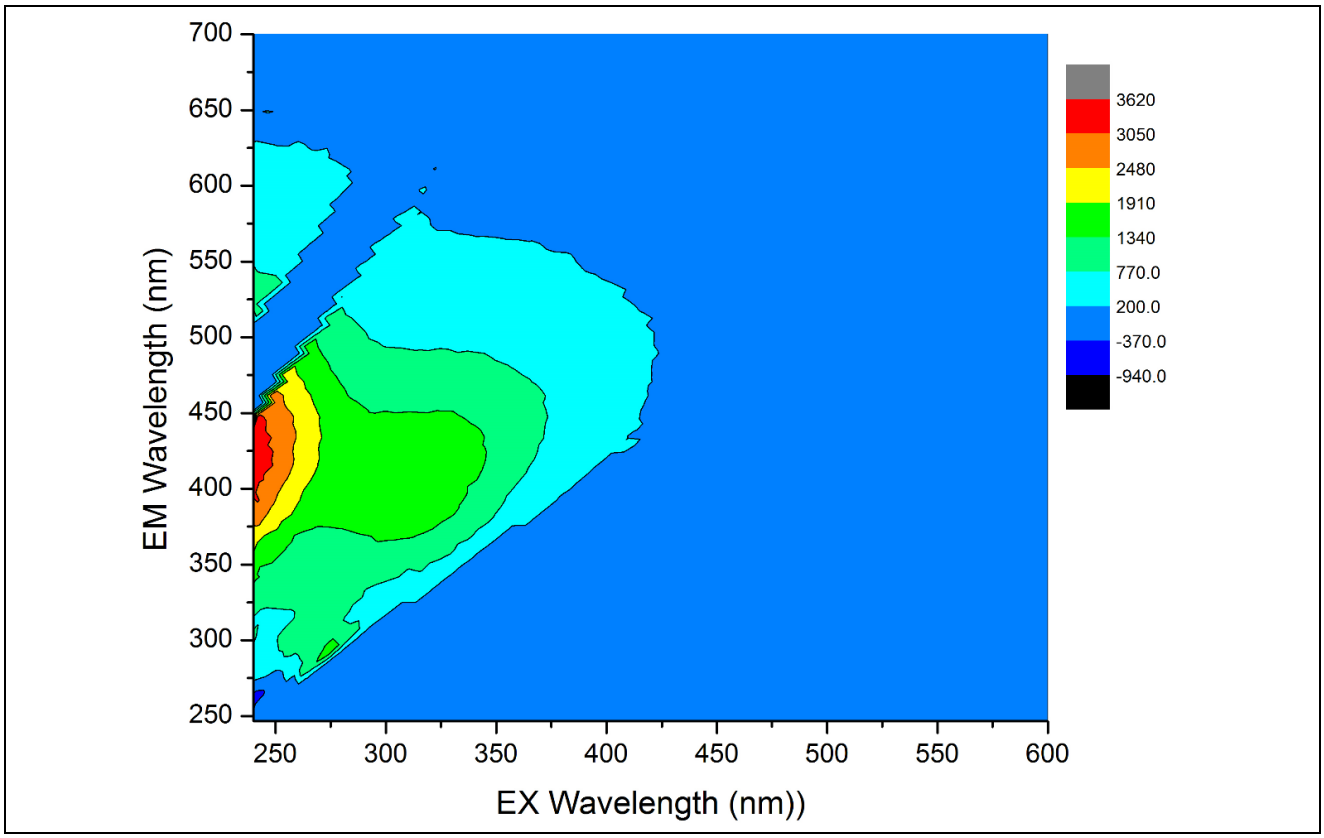


Figure C-12: FEEM on the source water TPI fraction before the THMFP test

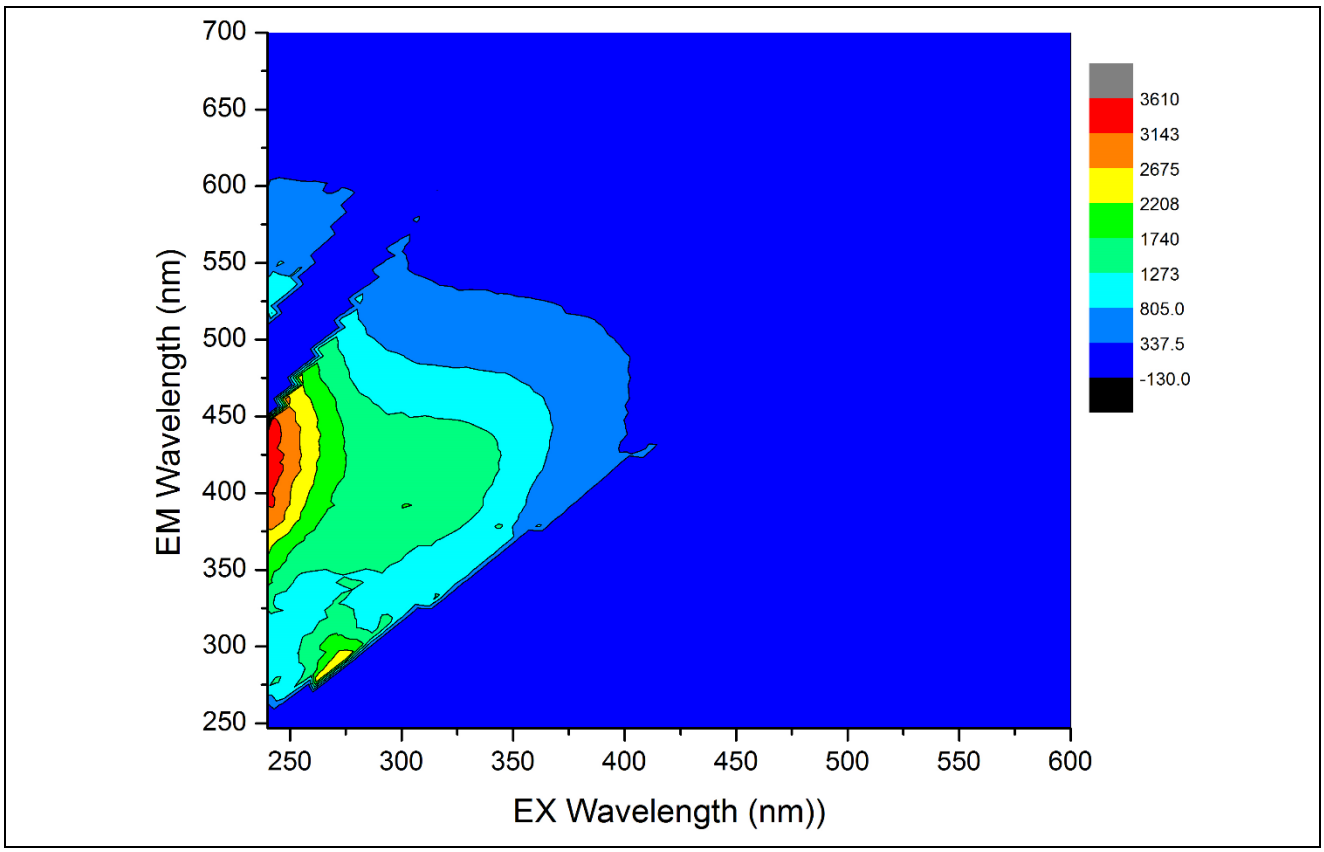


Figure C-13: FEEM on the source water TPI fraction on day 3 of the THMFP test

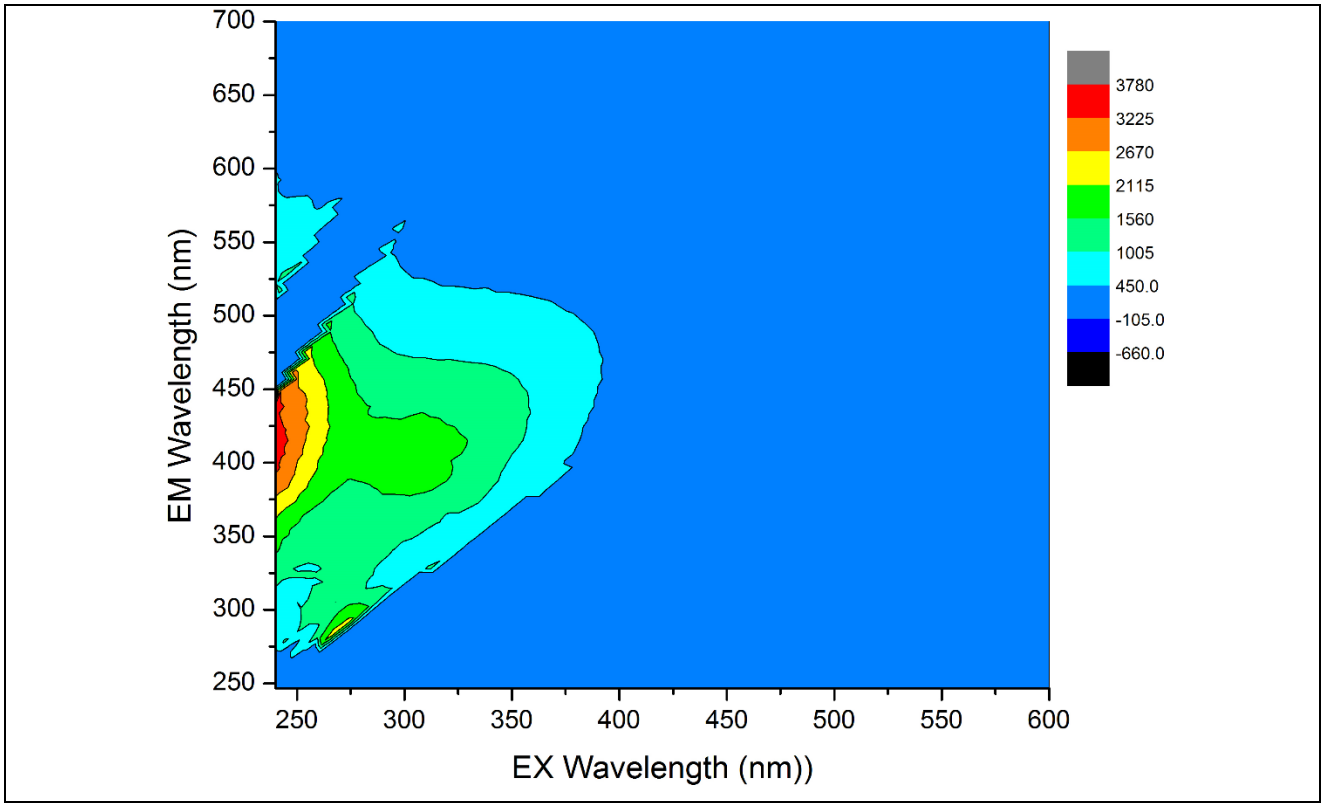


Figure C-14: FEEM on the source water TPI fraction on day 7 of the THMFP test

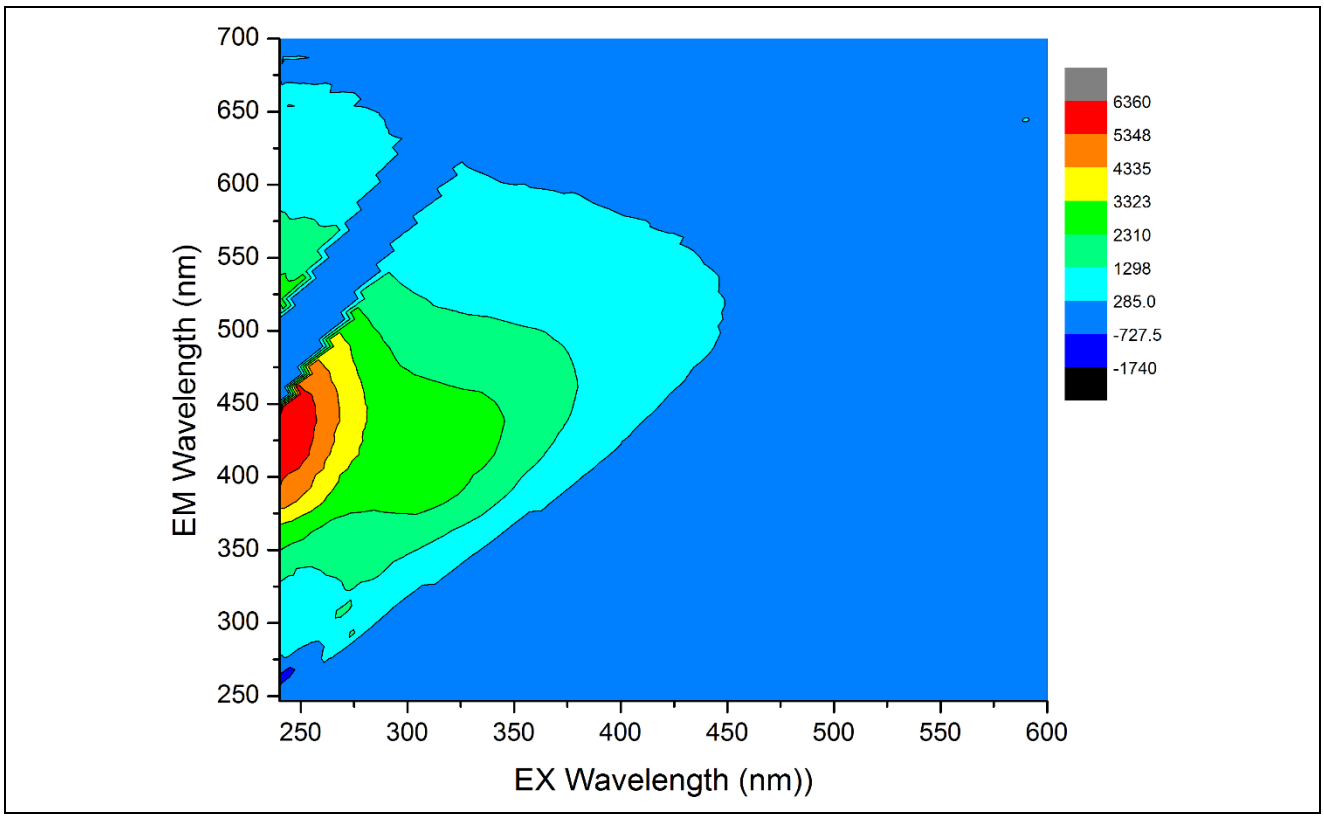


Figure C-15: FEEM on the treated water HPO fraction before the THMFP test

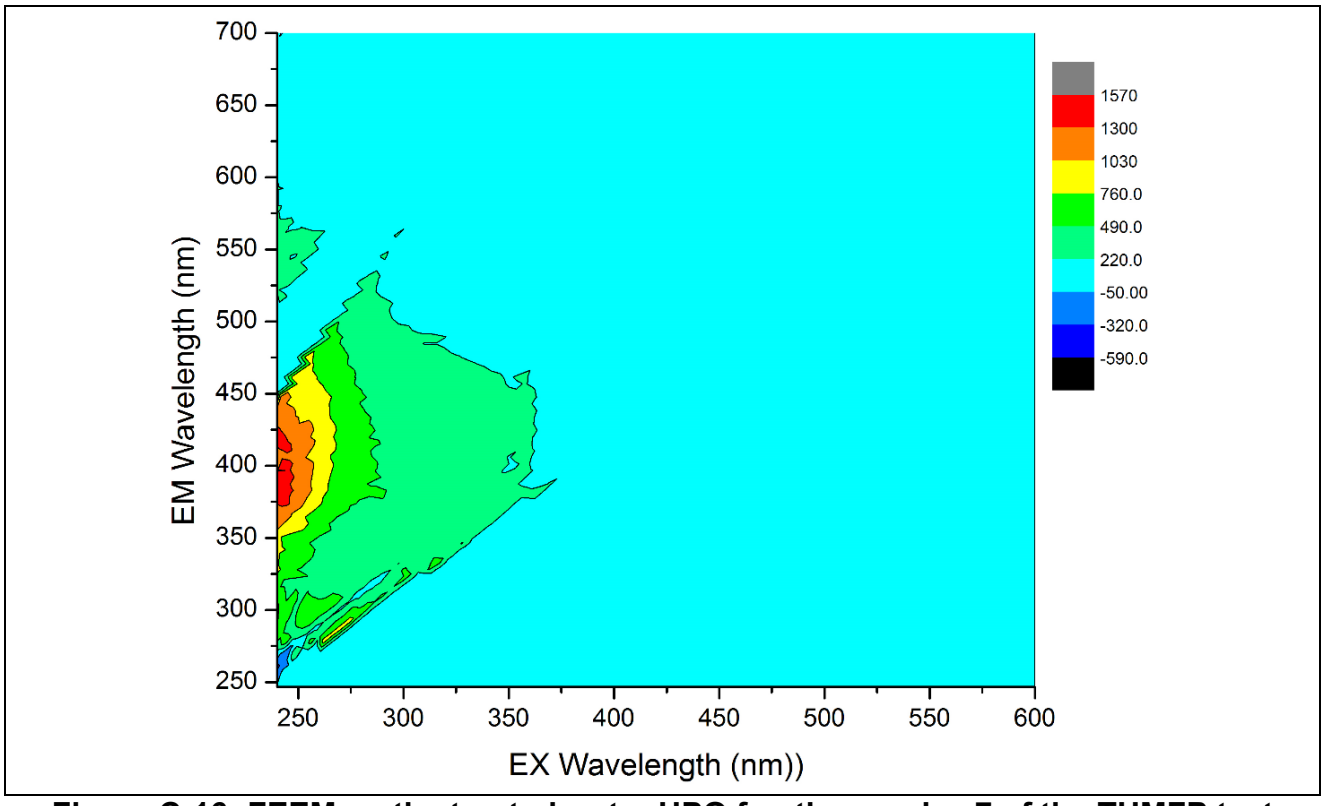


Figure C-16: FEEM on the treated water HPO fraction on day 7 of the THMFP test

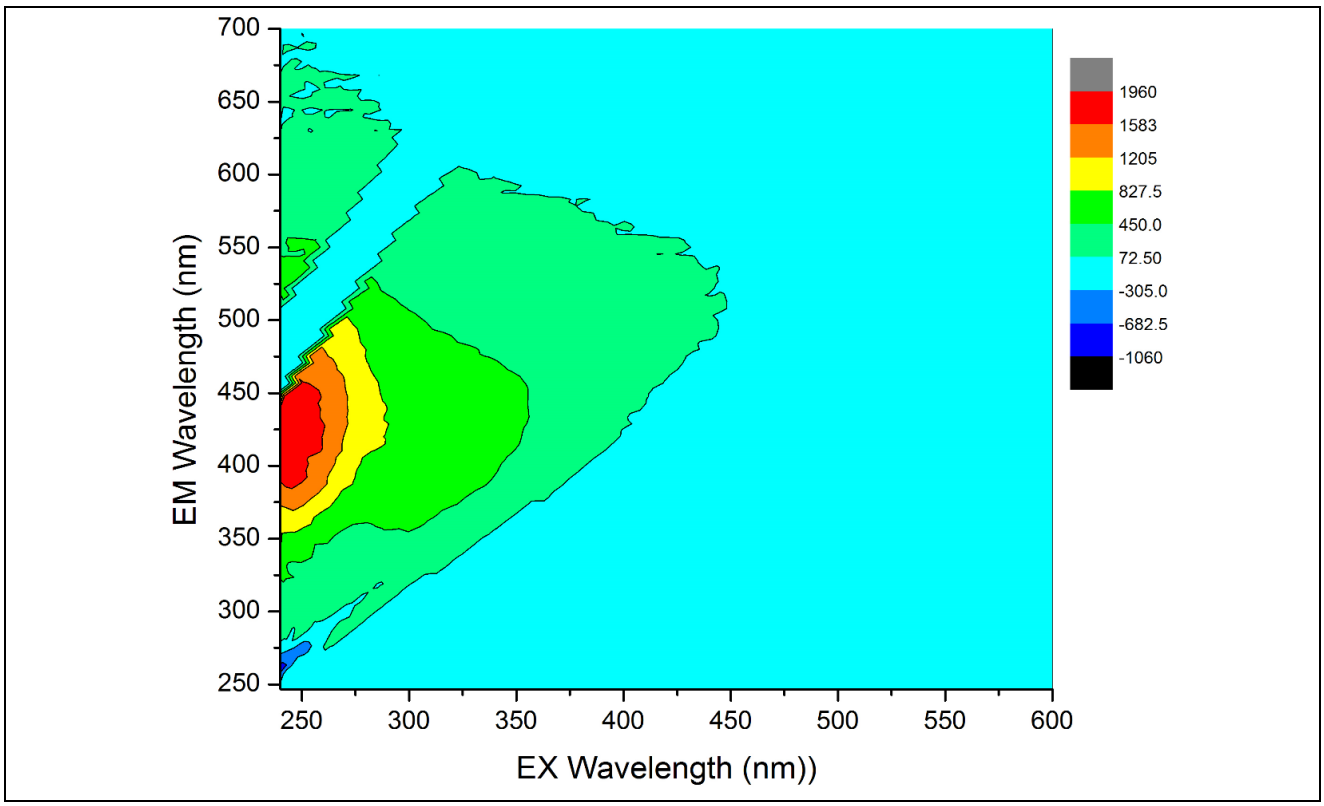


Figure C-17: FEEM on the treated water HPI fraction before the THMFP test

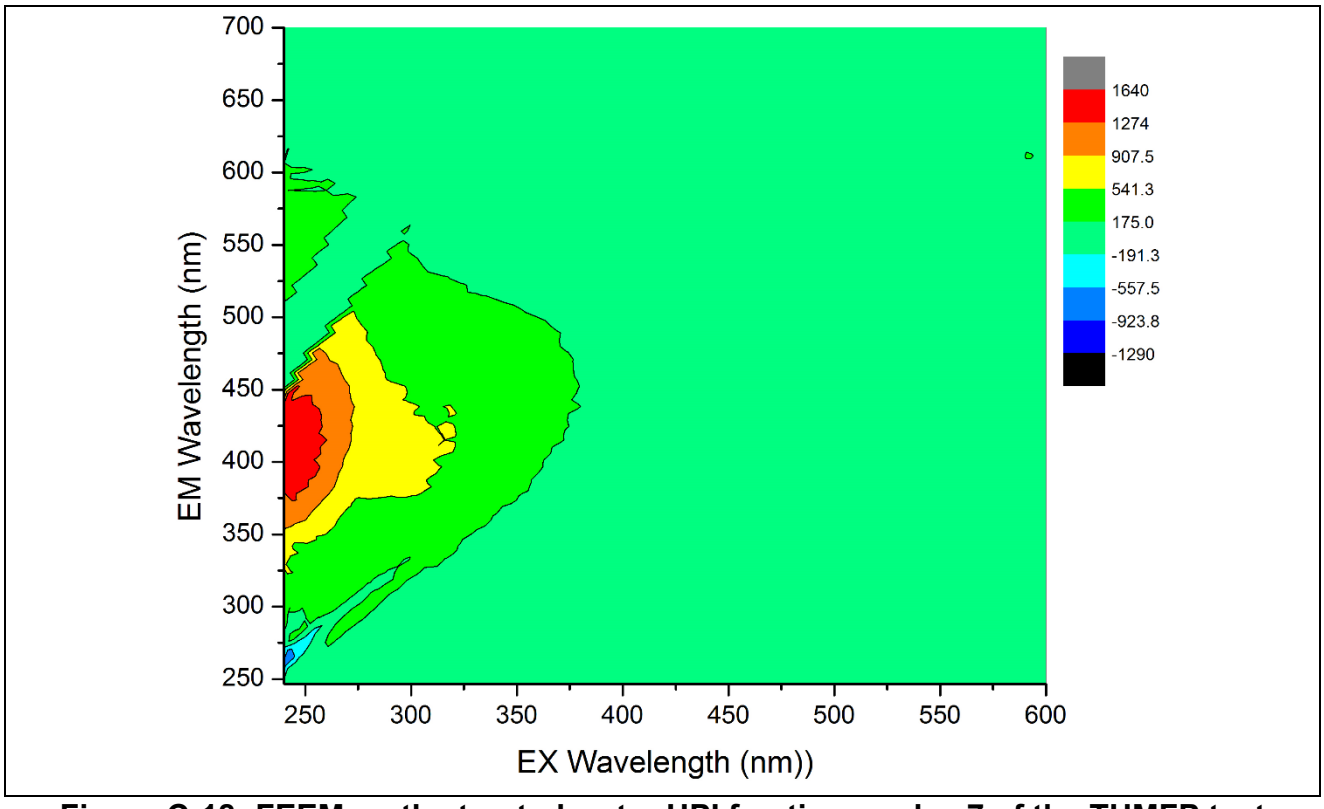


Figure C-18: FEEM on the treated water HPI fraction on day 7 of the THMFP test

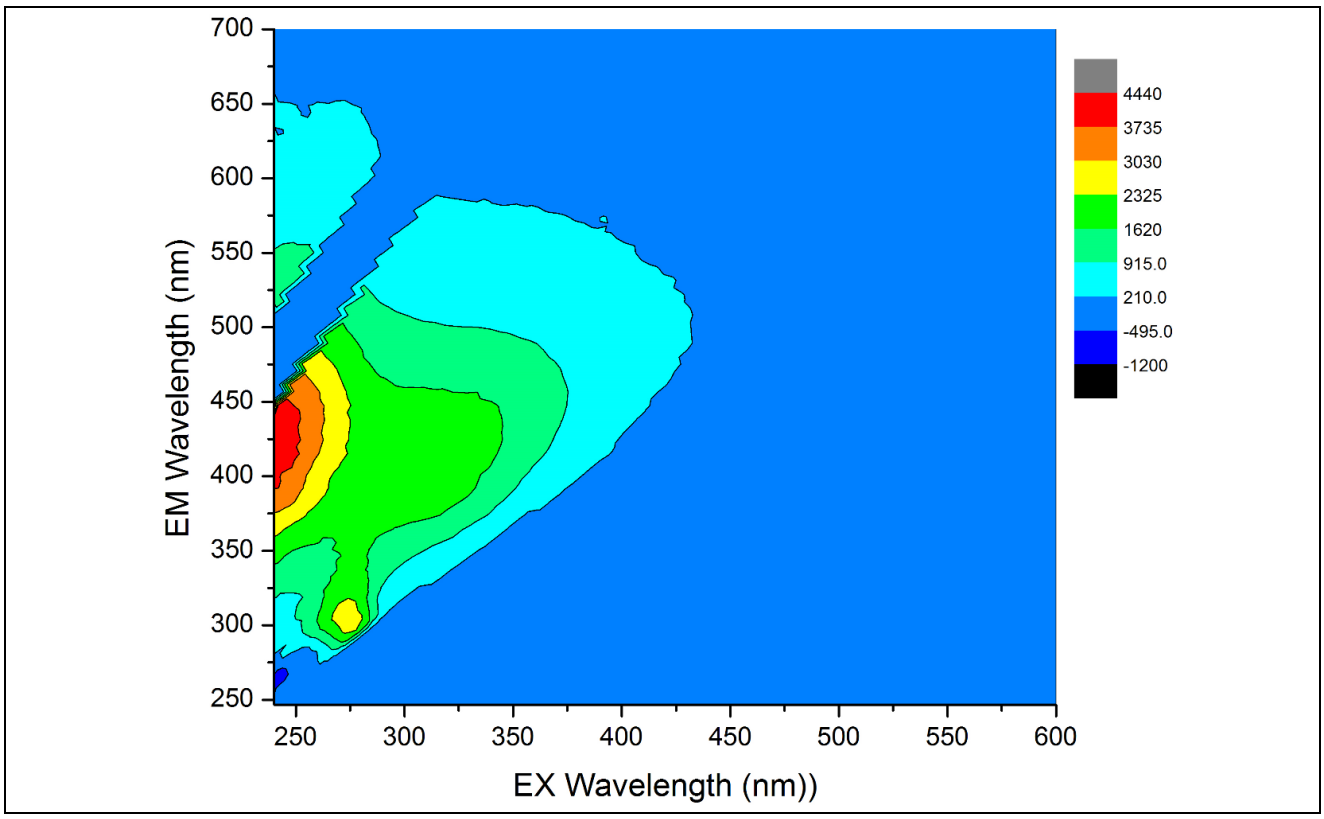


Figure C-19: FEEM on the treated water TPI fraction before the THMFP test

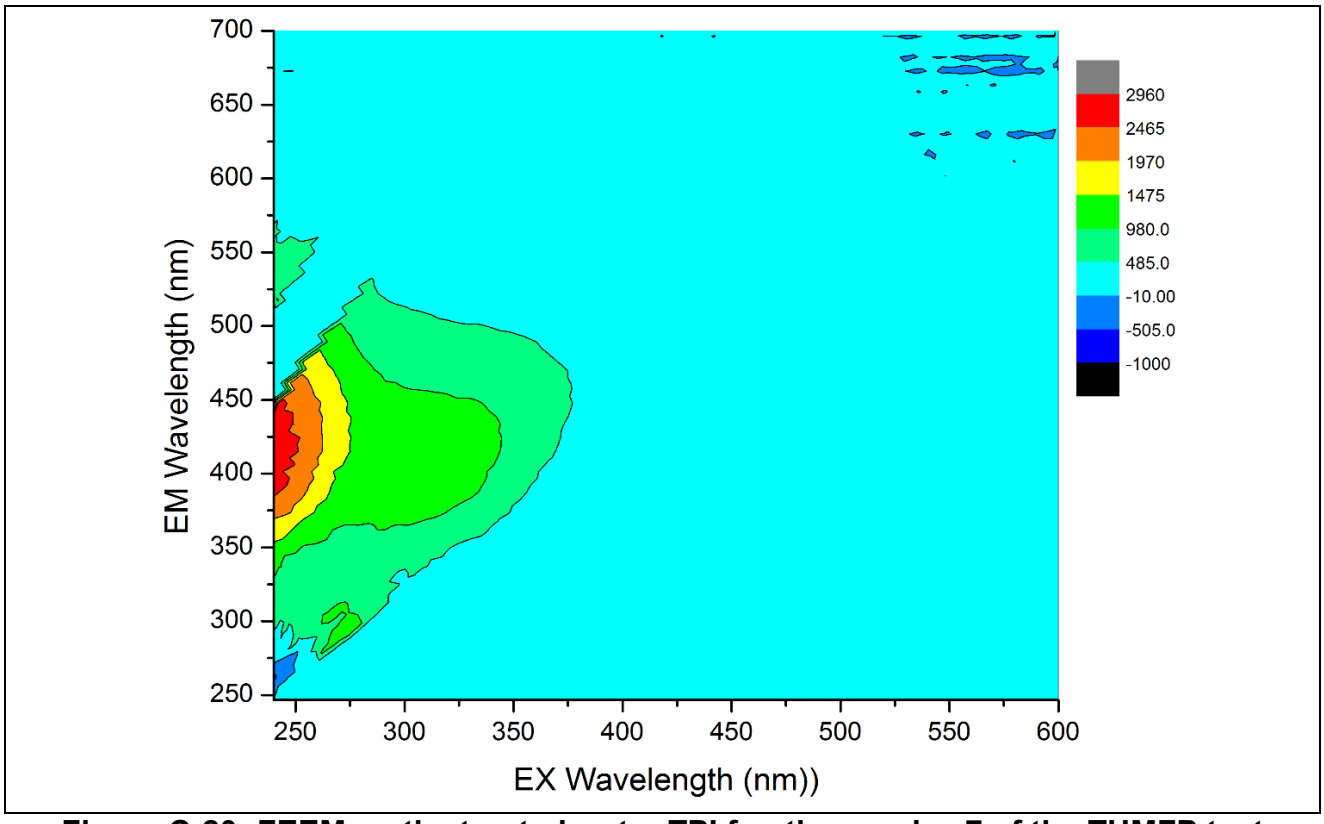


Figure C-20: FEEM on the treated water TPI fraction on day 7 of the THMFP test