IDENTIFICATION AND QUANTIFICATION OF NATURAL ORGANIC MATTER IN THE WINDHOEK OPERATING COMPANY WATER TREATMENT PLANT IN WINDHOEK, NAMIBIA

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Abstract

Natural organic matter (NOM) is a generic term for a mixture of organic, slightly water-soluble components found in soil, sediment and natural waters, which represents severe challenges for the process control in water treatment plants as well as water distribution systems. The effective removal of NOM during drinking water treatment requires a good understanding of its character. The current study aimed to identify and quantify NOM present in the Windhoek Goreangab Operating Company (WINGOC) water treatment plant and to assess the efficiency of the plant in removing or reducing these organic matters. Water samples were collected at different points in the treatment plant starting with the raw ponds until the final treatment point once a week over a period of twelve months. Temperature, pH, organic content, nitrates, UV absorbance at 254 nm (UV_{254}) and specific UV absorbance (SUVA) measurements were performed on the day of sampling. The molecular weight distribution of the organic fractions was determined using high pressure size exclusion chromatography (HPSEC) with fluorescence and UV detection methods.

Raw water (ponds) had high dissolved organic matter, however this was greatly reduced after the dissolved air flotation, biological and granular activated carbon treatment processes. Dissolved organic carbon (DOC) removal efficiencies of up to 98% were achieved in some cases, which indicates that the treatment process employed at WINGOC treatment plant is effective in removing organic matter from the water. UV absorbance at 254 nm was found to be directly correlated to the organic content, decreasing gradually as the water is passing through different treatment stages. The reduction in UV absorbance could be ascribed to the loss of aromaticity due to

depolymerisation of high molecular weight (HMW) organic matter, as is normally observed in samples of natural waters containing high levels of humic substances. Water samples had specific UV absorbance values ranging between 2.88 and 4.80 $Lmg^{-1}m^{-1}$ before ozonation, while these values were less than 2.38 $Lmg^{-1}m^{-1}$ after ozonation. From these values, it could be concluded that the NOM fractions at the WINGOC treatment plant contained complex mixtures of humic- and non-humic substances with varying sizes and degrees of hydrophobicity/aromaticity as can be deduced from the high UV absorbance and SUVA data obtained for the treatment stages before ozonation, and these were converted to hydrophilic, low molecular weight organics with low UV absorbance and SUVA values after the ozonation process. The UV and SUVA results were well supported by the molecular weight distribution data obtained in size exclusion chromatography. No clear trends could be deduced with regard to seasonal changes.

The findings of this study provided an improved understanding on the character and fate of NOM during different water treatment processes. However, since the results were obtained for the bulk water samples, future studies should involve fractionation of the NOM to enable identification of individual compounds. Size exclusion chromatography (SEC) in combination with mass spectrometry (MS), nuclear magnetic resonance mass spectrometry (NMR) and/or Fourier transform infrared spectroscopy (FTIR) would be helpful in the determination of the chemical composition of the NOM.

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List of abbreviations

AOC	Assimilable Organic Carbon
AOM	Algal Organic Matter
ASTM	American Society for Testing and Material
AER	Anionic exchange resins
BDOC	Biodegradable Dissolved Organic Carbon
DBPs	Disinfection By-products
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
FA	Fulvic Acid
FRI	Fluorescence regional integration
F-EEM	Fluorescence Excitation Emission Matrix
FL	Fluorescence
FLD	Fluorescence Detection
FTIR	Fourier Transform Infrared
GAC	Granular Activated Carbon
GC-MS	Gas Chromatography–Mass Spectrometry
HA	Humic Acid
HMW	High Molecular Weight

HS	Humic Substances
LMW	Low Molecular Weight
MIEX	Magnetic ion exchange
MS	Mass Spectrometry
MWD	Molecular Weight Distribution
NGWRP	New Goreangab Water Reclamation Plant
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
NO_3	Nitrates
PAC	Powdered Activated Carbon
PARAFAC	Parallel Factor Analysis
PCA	Principal Component Analysis
PLS	Partial Least Squares
POC	Particulate Organic Carbon
SEC	Size Exclusion Chromatography
SUVA	Specific Ultraviolet Absorption
THM	Trihalomethane
TOC	Total Organic Carbon
URI	Uniform Resource Identifier

UV_{254}	Ultraviolet Absorption at 254 nm
UV-Vis	Ultraviolet-Visible
WINGOC	Windhoek Goreangab Operating Company

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Declarations

I, Hilya Kauna Sakaria, hereby declare that this is my own work and is true reflection of my research, and that this work, or any part thereof has not been submitted for a degree at any other institution.

……	……	……
Name of student	**Signature**	**Date**

1. INTRODUCTION

1.1 Background of the study

Namibia is an extremely arid country and receives only about 360 millimeters of rainfall annually. Most parts of Namibia are currently facing a water supply crisis due to poor rainfall received in the country over the past few rainy seasons. The central area of Namibia, in particular, has been faced with water supply challenges over the years due to low rainfall and increased pollution of some of its major water sources. This is more critical for the capital city, Windhoek, which has been experiencing a steady population increase each year, and consequently, a high demand for potable water.

To circumvent this, the City of Windhoek (Windhoek municipality) explored various options such as groundwater recharge, desalination of groundwater from the northern water table, trucking water into Windhoek, fog-harvesting, etc, to make more water available, however all these options were deemed economically impractical (2). Therefore, a potable water reclamation plant was finally chosen as the best practical option, both in terms of cost and sustainability, leading to the commissioning of a water treatment plant by the City of Windhoek in 1969 (3; 4). This plant had an initial capacity of 1.7 Mm^3/year and contributed greatly to the supply of drinking water for the city, and it has been undergoing numerous upgrades, finally attaining a supply capacity of 2.7 Mm^3/year in 1995. However, the demand for water kept increasing due to the rapid population growth in the city (5). In 2002, the new Goreangab water reclamation plant (NGWRP) was built with a capacity of 7.6 Mm^3/year (2). This new plant now supplies a significant amount of potable water required by the City of Windhoek. Without this

plant, sustainable water access would be unavailable to many parts of Windhoek as the water demand for the City exceeds the natural water supply limit (3).

The City of Windhoek, along with Namibia Water Corporation Limited (NamWater and Windhoek Goreangab Operating Company (WINGOC) are the key organisations that work together to produce potable water for the city. The City of Windhoek, through its wastewater treatment plant (Gammams water care works), supplies semi-treated, recycled domestic water (the so-called grey-water) to the WINGOC treatment plant. WINGOC is sub-contracted by the City of Windhoek to maintain the plant and treat the grey-water to a specific standard. The water from WINGOC (30%) is then blended with 70% of the water from natural sources (which is supplied by NamWater) before it is sent to the reservoirs for distribution to the residents (2).

Although water reclamation has been taking place in Windhoek for more than 40 years, numerous challenges continue to haunt the treatment plants (3). One such challenge is the presence of natural organic matter (NOM) in the water, which presents severe challenges for process control in water treatment and distribution systems (6). For example, NOM contributes to colour, taste and odour in the water, foul membranes, block filtration pores and compete for adsorption sites on the activated carbon beds used in water treatment, thus reducing their capacity to remove organic micropollutants, and may lead to the formation of disinfection by-products (DBPs), such as the trihalomethane (THM) species (7). Therefore, NOM negatively impacts water treatment processes, increase the demand for coagulants and disinfectant doses, and consequently, increase the operation cost of water treatment plants (4; 8; 1). In the water distribution networks, NOM influences corrosion and the biodegradable fraction of NOM may promote microbial growth in

water distribution networks, particularly in systems which do not maintain a disinfectant residual in the distribution network (8; 9).

1.2 Statement of the problem

In order to minimise the undesirable effects described above, it is essential to limit the amount of NOM in the drinking water treatment plants. The efficiency of drinking water treatment is affected by both the amount and composition of NOM. Furthermore, the types of DBPs that may be formed during oxidation processes are influenced by the nature of NOM present. However, there is limited knowledge regarding the selection and operation of treatment processes for the removal of specific DBP precursors rather than of bulk NOM (7). Biological stability of drinking water, which is the capacity of the water to minimise microbial growth in the distribution system, is influenced by specific fractions of biodegradable organic matter which may be present in very low concentrations. These low molecular weight organics, referred to as assimilable organic carbon (AOC), may be quantified using bioassay methods (10). However, the current bioassay methods are not only incapable of detecting and quantifying the full spectrum of microbes promoting NOM, but are also laborious and time consuming (11).

By systematically characterising NOM, the problematic fractions can be identified and targeted for removal and transformation. Therefore, proper characterisation of the NOM in raw water or after different treatment steps would be an important basis for the selection of water treatment processes, monitoring of the performance of different treatment steps, and assessing distribution system water quality.

1.3 Objectives of the study

The primary aim of this project was to develop suitable methods for the identification and quantification of various natural organic matter (NOM) present in the WINGOC water treatment plant and to identify cost-effective methods for their removal. In order to achieve the main aim, this project had the following specific objectives:

a. To assess the levels of nitrates (NO_3^-), dissolved organic carbon (DOC), ultraviolet absorption at 254 nm (UV_{254}), pH and specific ultraviolet absorption (SUVA) within the process train and establish the relationship between these parameters and the organic matter.
b. To identify the NOM present at different stages in the WINGOC water treatment plant using size exclusion chromatography (SEC) in combination with ultraviolet-visible (UV-Vis) and fluorescence (FL) detection methods.
c. To assess the efficiency of the plant in removing or reducing organic matter.

1.4 Significance of the study

As discussed in **Section 1.2**, the presence of NOMs in water is often accompanied with increased water treatment costs. Establishing methods of reducing or removing NOM from water would therefore reduce the water treatment operational costs significantly. Availability of methods for monitoring or removing NOM in the treatment plants will facilitate the process of ensuring that the water is safe for consumption. Regular monitoring of NOM levels in the water will serve to inform water supply utilities as to when necessary measures need to be taken.

This research improved the understanding of the character and fate of NOM during different drinking water treatment processes using bulk NOM water qualities (UV_{254}, SUVA and DOC) and various NOM characterisation tools (fluorescence excitation

emission matrix (F-EEM), SEC with UV). These complementary techniques could provide information on the fate of NOM fractions that negatively impact treatment efficiency, promote biological re-growth in water distribution systems and provide precursors for DBPs in systems that use oxidation/disinfection processes. This information is useful in improving the design of water treatment processes and stages by targeting the removal of specific NOM fractions, resulting in the reduction of DBP formation, as well as chemical and energy uses during water treatment. The results could also be used for improving process control of water treatment plants and offer the possibility for online monitoring of NOM at low levels of detection, which is otherwise not feasible with only DOC or UV_{254} measurements.

1.5 Limitations of the study

The study relied on good analytical tools, some of which were not available, to allow for accurate determination of NOM present at different points in the treatment plant. The data collection time was limited as only data collected over a period of one year were used, which does not allow reliable assessment of the seasonal variations on the organic matter.

2. LITERATURE REVIEW

2.1 Natural organic matter: Definition, origin and classification

Natural organic matter (NOM) is a generic term used for complex mixtures of organic, slightly water-soluble components found in soil, sediment and natural waters, which contribute to the brownish-yellowish colour of natural waters. These compounds come from composting activities of microbes on dead plant tissues, dead organisms and excrement of living organisms.

NOM are structurally diverse molecules and their composition depends mainly on the origin of the material and the amount of modification it has undergone (1; 11). For example, NOM that is derived from aquatic algae has relatively high nitrogen, low aromatic carbon and phenolic contents, while a terrestrially derived NOM has relatively low nitrogen content but large amounts of aromatic carbon and phenolic contents (12). The aromatic fraction of NOM has been found to be the main reactive component, and it varies with sources. NOM, in general, can be divided into two main types based on the source (8; 13):

1) Allochthonous NOM – This type of NOM comes from the breakdown of terrestrial biomass or through soil leaching in the watershed, mainly from runoff or vegetative debris, hence the production and characteristics of this type of NOM is related to vegetative patterns as well as hydrologic and geological characteristics of the watershed.

2) Autochthonous NOM – This type of NOM comes from *in-situ* sources, mainly algal organic matter (AOM) and other phytoplankton and macrophytes. These could be extracellular or intracellular organic matter consisting macromolecules and cell

fragments. The production of this type of NOM is therefore related to photosynthetic activity and decay products of algal matter.

NOM present in drinking water sources usually contain both humic (non-polar) and non-humic (polar) material (4). Hydrophilic (non-humic) fractions of NOM exhibit some of the properties typically observed for classic humic fractions of low molecular weights (14). Aquatic humic substances (HS) can be divided into two main fractions: humic acids (HA), which are insoluble at pH less than 1, and fulvic acids (FA), which are soluble at all pHs (**Figure 2.1**). Humic substances are complex macromolecules some of which consist of a mixture of many organic acids containing carboxylic and phenolic functional groups. Aquatic HS account for approximately half the overall percentages of the DOC present in most natural waters. The non-humic fraction of NOM consists of hydrophilic acids, proteins, amino acids, amino sugars and carbohydrates. FA and HA form complexes with metal ions such as Cd^{2+}, Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Pb^{2+} and Zn^{2+}. The chelation of these metal ions to humic substances is possible through the phthalic and salicylic acid moieties in these humic substances. Due to such complexation, toxic metals bound to humic substances can remain in a bioavailable state in environmental waters. Complexation transfers toxic metals into the aquatic environment and hence NOM may contribute to toxicity of metals present in water (7; 15).

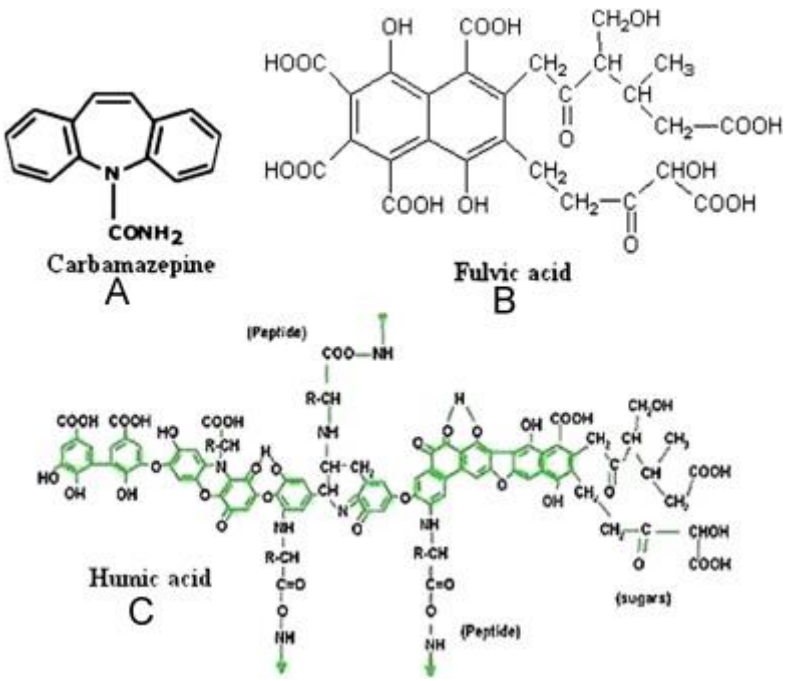


Figure 2.1 Typical examples of fulvic and humic acids *(1)*.

2.2 Effects of NOM

Over the past two decades, increasing NOM concentrations have been observed in water sources in many countries due to issues such as global warming, changes in soil acidification, increased drought severity and intensive precipitation events (6; 10). The presence of NOM in water significantly impacts different drinking water treatment processes as well as water quality in the distribution system, leading to operational problems and increased cost of water treatment (6; 12). Some of the ways in which NOM affects drinking water quality and the performance of water treatment process are summarised below (7):

(i) NOM impacts aesthetic drinking water quality by affecting colour, taste and odour to the water.

(ii) NOM increases the demand or dose of coagulants, oxidants and disinfectants required for drinking water treatment.

(iii) NOM present in water may react with chlorine or other disinfectants/oxidants to produce potentially harmful disinfection by-products (DBPs), many of which may be carcinogenic or mutagenic.

(iv) NOM is responsible for fouling of membranes, reducing the flux, resulting in high frequency of backwashing and cleaning of membranes to restore the flux.

(v) NOM competes with target organic micropollutants for adsorption sites in activated carbon filters, adversely impacting both adsorption capacity and adsorption kinetics of the target organic micropollutants.

(vi) Presence of biodegradable NOM in water entering the distribution system may lead to biological regrowth, when a sufficient disinfectant residual is not maintained in the distribution system.

(vii) Some NOM fractions may promote corrosion at low pH, whereas some studies have shown that NOM decreases the rate of corrosion of iron pipes at high pH in the distribution system.

2.3 Methods for the analysis of NOM in water

2.3.1 Sampling and sample pre-treatment

Sampling for NOM analysis should follow appropriate standard procedures such as those specified by the World Health Organisation (WHO) and American society for testing and material (ASTM) for water testing (10), which provides detailed instructions for preparation of the sample container, sampling, sample preservation and analysis of samples. For reliable analysis of the samples, these four basic steps (preparation of the sample container, sampling, sample preservation and analysis of samples) should be performed according to the procedures specified. External contamination during handling should be avoided as much as possible and for samples rich in biodegradable organic

matter, rapid analysis should be carried out to minimise biodegradation and hydrolysis of some components of NOM. Samples that cannot be analysed immediately after sampling should be stored at a temperature of 4°C or below.

Samples for DOC analysis are generally filtered through 0.45 μm porous membrane filters immediately after sampling. This filtration step also provides physical sterilisation of the sample through removal of suspended solids (16; 17). It is necessary to use cooling boxes for the shipment of samples. The shipment method should consider the arrival time for the sample and the time between sampling and analysis. Non-cooled samples should be analysed within 24 hours after sampling, cooled samples can be stored up to 72 hours.

2.3.2 Analytical approaches

Determining the exact nature and composition of organics present in a water sample can be quite a challenging and costly process. Various analytical approaches are currently employed in the characterisation of NOM fractions in water including those that are applied to bulk samples (UV-visible spectrophotometry and fluorescence spectroscopy) and to the separation and identification of individual compounds or compound classes (size exclusion chromatography (SEC), mass spectrometry (MS), nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy). This section provides a brief overview of the analytical techniques used to characterise NOM in water.

2.3.2.1 UV-Visible spectrophotometry

NOM absorbs light over a wide range of wavelengths, from UV to visible light. As such, UV/Vis absorbance by NOM is a semi-quantitative indicator of the NOM concentration in natural waters. UV light absorbance at 254 nm (UV_{254}) is widely used in water

treatment plants to monitor the concentration of DOC (14). These UV absorbing chromophores are associated primarily with the humic fraction of NOM (7). The reactivity of DOC and aquatic humic substances with oxidants, such as chlorine and ozone depends strongly on the aromaticity of the organic matter (12).

SUVA provides a simpler method for estimating aromaticity of DOC in a water sample. SUVA is an "average" absorptivity for all the molecules that comprise the DOC in a water sample, therefore it is considered as a valuable parameter to evaluate DOC aromaticity and treatability (11; 13; 16). SUVA is defined as the ratio of the sample's UV absorbance at 254 nm to the DOC concentration of the solution, which is calculated according to **equation 2.1** below (13):

$$\mathrm{SUVA} = \left(\frac{\mathrm{UV}_{254}\left(\mathrm{cm}^{-1}\right)}{\mathrm{DOC}\left(\mathrm{mgL}^{-1}\right)} \right) \times 100 \qquad (2.1)$$

There is a high correlation between SUVA and the aromatic contents of many NOM fractions (11). Water with a high concentration of hydrophobic NOM such as humic substances have a high SUVA value, which can be used to estimate the chemical characteristic of DOC in a given environment (11). A SUVA of ≤ 2 indicates presence of mostly lower molecular weight, less aromatic and relatively low hydrophobic non-humic NOM, while SUVA between 2 and 4 indicates a mixture of varying molecular weights of aquatic humics, hydrophobic and hydrophilic NOM, and other NOM (**Table 2.1**) (13; 18).

Table 2.1: Guidelines on the nature of DOC based on SUVA values *(8)*.

SUVA ($Lmg^{-1}m^{-1}$)	**NOM composition**
> 4	Mostly aquatic humic material High hydrophobicity High molecular weight
2 – 4	Mixture of aquatic humics and other NOM Mixture of hydrophobic and hydrophilic NOM Mixture of molecular weights
< 2	Mostly non-humics Low hydrophobicity Low molecular weights

2.3.2.2 Fluorescence spectroscopy

Fluorescence spectroscopy is widely used to characterise NOM fractions which fluoresce when excited by UV and blue light (8). In fluorescence measurements, a sample is excited by a light source (such as a xenon arc lamp) and the emitted light is recorded. An excitation emission matrix (EEM) is obtained by collecting the emission spectra at a series of excitation wavelengths. Fluorescence characterisation typically involves the use of excitation-emission wavelength pairs to identify fluorophores based on the location of fluorescence peaks on EEM contour plots (8; 18). In the case of NOM, EEMs are used to identify two main fluorophores (light emitting species): humic-like and protein-like fluorophores (8). Based on 3-D EEM, humic substances exhibit a characteristic fluorescence intensity maximum over the excitation and emission ranges of 300-350 nm and 400-450 nm, respectively, while proteins exhibit a characteristic fluorescence intensity maximum over the excitation and emission ranges of 250-300 nm and 300-350 nm, respectively (8).

Because of its high specificity, fluorescence detection can be used to selectively monitor for specific components of interest, either humic-like or protein-like NOM components, based on their respective EEM spectra. Fluorescence detection is, however, inefficient for saccharides as they do not fluoresce (8).

The fluorescence intensity and characteristics normally depend on the concentration and composition of NOM, as well as other factors such as pH, temperature and ionic strength of the water (8). Fluorescence intensity is also known to increase with DOC, but due to the absorbance characteristic of different DOC molecules, the increase may not be linear, especially at higher concentrations (7; 18). Other light absorbing molecules or ions such as nitrates may also cause a reduction of the measured intensity. To account for these inner-filter effects, absorbance corrections are usually applied, however these corrections may not be necessary if the sample absorbance is less than 0.05 or if the DOC concentration of the sample is diluted to about 1 mg C/L prior to measurement (4). Water samples are also normally acidified to pH ~3 prior to measurement in order to minimise metal-binding by dissolved organics, however this may also lead to significant reduction in fluorescence intensities and loss of resolution for the more pH sensitive EEM peaks such as the protein-like peaks located at excitation/emission wavelengths of 250/320 nm, respectively (12).

Other methods including fluorescence regional integration (FRI) (8), multivariate data analysis (e.g. principal component analysis, PCA, and partial least squares regression, PLS) (8) and multi-way data analysis using parallel factor analysis (PARAFAC) are also useful in the analysis of F-EEMs data (8). PARAFAC has been used to decompose F-EEMs into individual components some of which have been attributed to protein-like or humic-like NOM (18).

2.3.2.3 Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) is a high performance liquid chromatographic (HPLC) separation method in which the chromatographic column packing consists of precisely controlled pore sizes and the sample is fractionated according to its size or hydrodynamic volume. Larger molecules pass through without being retained and smaller molecules penetrate the pores of the packing particles and elute later. Hence, SEC chromatography can be used to fractionate NOM in a given sample according to the size of components from higher to lower, thus providing a MW or molecular size (MS) distribution. The data obtained can be represented as a SEC chromatogram in terms of either retention time or MW distribution (in Daltons, Da) if calibration chemicals are used. The peaks depicted in these chromatograms give an indication of the MW or MS of different components of NOM including polysaccharides (consisting of macromolecules such as polysaccharides and proteins), humic substances, building blocks (hydrolysates of humic substances), low molecular weight (LMW) acids and neutrals, and amphiphilic compounds.

Chromatography has been widely used in MW/MS determinations of NOM in combination with UV detection (18). While UV detection is effective for humic substances, it is less effective (or ineffective) for non-humic components of NOM such as proteins and saccharides (simple sugars and polysaccharides) due to lack of suitable chromophores (14). Other factors such as charge, molecular structure, steric effects and hydrophobicity may have an influence on the results. SEC coupled with fluorescence and variable wavelength UV detectors (which have long been used in traditional analysis of specific organic compounds) can be used for NOM analysis. This permits differentiation between NOM components that exhibit high UV absorptivity at 254 nm and other NOM

components that are more sensitively detected at other UV wavelengths – e.g. 210 nm for amino acids and proteins. While humic substances are characterised by a uniform resource identifier (URI) of 1.5 to 2.0, proteins and their amino acid building blocks show higher URI values of 5 to 10 (12). Coupling a fluorescence detector sequentially with SEC facilitates identification of separated compounds on the basis of their excitation and emission wavelengths.

2.3.2.4 GC-MS, FTIR and NMR

Detailed characterisation of individual organic matter in natural waters is often achieved through the use of more powerful analytical techniques such as gas chromatography–mass spectrometry (GC-MS), FTIR and NMR. FTIR has been widely used for characterisation of humic substances in water samples and provides valuable information on the structural and functional properties of NOM molecules (10). Differences in the relative intensities of some absorption bands are often used to assign major spectral bands, which may, in turn, give an indication of the types and kinds of chemical and elemental bonding in the NOM. The most direct measurement of aromaticity of NOM is provided by ^{13}C NMR spectroscopy but it requires expensive, sophisticated instrumentation and significant sample preparation (8).

It is worth mentioning that the choice of the analytical method normally depends on the nature/goal of the research, these detailed analyses are only required in cases where chemical information of individual NOM is necessary, otherwise characterisation using bulk water methods is less costly and can provide important water quality information.

2.4 Methods for the removal of NOMs in water

The removal of NOM during water treatment depends on the characteristics of the NOM present (e.g. molecular weight distribution (MWD), carboxylic acidity and humic substances content), its concentration and the removal methods applied (1). High molecular weight (HMW) NOM is easier to remove than low molecular weight NOM (MW < 500 Da) (9; 18). NOM components with high carboxylic functionality and high density are generally more difficult to remove by conventional treatment (4). Several water treatment methods are used to remove NOM during water treatment with different degree of success and some of these methods are briefly discussed below.

2.4.1 Enhanced coagulation

NOM removal in a conventional water treatment process may be achieved through the addition of chemical coagulants such as ferric chloride ($FeCl_3$) and aluminium chloride ($AlCl_3$). Conventional water treatment involving coagulation, flocculation and sedimentation is normally used for the removal of turbidity in raw water. Removal of NOM requires enhanced coagulation with coagulant doses 5-100 mg/L (for aluminium (Al) and iron (Fe) salts) higher than what would be required for turbidity removal (2.5 mg/L). However, the increased coagulant dose may lead to increased sludge production and costs of treatment, especially for low alkalinity waters (18).

Coagulation with Al and Fe salts has been found to be effective in the removal of NOM (measured in terms of DOC), with efficiencies ranging between 25 to 70% (7; 10; 18). Because of the high DOC content, coagulation has proven to be effective in the removal of the hydrophobic fraction and high molecular weight NOM as opposed to the hydrophilic fraction and low molecular weight NOM compounds (10). The former is

composed of primarily humic substances which are fulvic and humic acids, and they are rich in aromatic carbon and phenolic structures, while the latter is composed mostly of aliphatic and nitrogenous organics such as carboxylic acids, carbohydrates and proteins (16). High SUVA values are expected for enhanced coagulation for waters with hydrophobic and relatively high molecular weight NOM. Conversely, enhanced coagulation is found to be ineffective for waters with more hydrophilic and low molecular weight NOM, as well as for waters with low DOC concentrations (< 2.0 mg C/L) and SUVA values (< 2.0), therefore additional NOM removal treatment would be recommended (16).

2.4.2 Activated carbon

Activated carbon (AC) is widely used to remove trace organic compounds from drinking water. It is an effective adsorbent for a wide range of undesirable organic compounds (e.g. pesticides as well as taste and odour compounds) which are often targeted for removal in drinking water treatment (18). It has also been found to be effective in the removal of NOM, although NOM competes for adsorption sites with the target compounds (18). AC may be used as granular activated carbon (GAC) or powdered activated carbon (PAC). GAC filters remove organic carbon through adsorption and biological degradation. In biologically active GAC filters, biodegradation is the main mechanism of organic carbon removal and the filters are made active by the absence of disinfection residual which would prevent formation of biomass that consumes the biodegradable organic carbon. In these filters, ozonation is often used prior to the GAC filters in order to degrade recalcitrant organic matter and promote biodegradation of the more biodegradable ozonated organic carbon. PAC is commonly applied in water treatment to remove NOM that cause odour and tastes and also to remove synthetic

organic chemicals. Application of PAC reduces the levels of AOC (7), and addition of PAC to a solids clarifier has been found to remove significant amounts of AOC compared to conventional settling tanks (11). PAC is also widely used prior to ultrafiltration (UF) to remove NOM and minimise fouling of UF membranes.

Adsorption of NOM by AC is controlled predominantly by the relationship between the molecular size distribution of NOM and the pore size distribution of the AC (11). Many studies have shown that due to a size exclusion effect, LMW organic matter could adsorb more onto the AC than HMW organic matter (4). When enhanced coagulation cannot sufficiently remove NOM, additional treatment by GAC filtration has been found to be effective in lowering the levels of organic carbon in the final water (7; 18).

2.4.3 Ion exchange

Ion exchange (IEX) is an effective method for removing NOM in water containing LMW humic substances, which are not effectively removed by coagulation (7). Ion exchange by electrostatic interaction is the dominant mechanism of NOM removal by IEX resins but hydrophobic interactions between the organic matter and the resin matrix can also have a significant effect on the removal of specific NOM fractions (1). The removal of NOM by anionic exchange resins (AER) is influenced by the characteristics of the resins such as strong or weak base AER, water quality (pH, ionic strength, hardness, etc.) and the character of NOM (molecular weight, charge density, polarity). Since most NOM components are negatively charged, macroporous AER are effective for NOM removal. Magnetic ion exchange (MIEX) resins, which are similar to conventional resins but 2 to 5 times smaller (less than 180 nm) in size, were also recently introduced. Their smaller size provides a larger surface area that enhances NOM removal and improves regeneration

efficiency, making it easier for NOM to diffuse in or out of the resin (10; 11). The resins are used in a continuously stirred contactor similar to a flash mixer in a conventional water treatment plant in order to overcome the high head loss and problems of backwashing associated with the small size of the resins (12). MIEX can remove 30 - 70% of the DOC depending on the water quality (18; 19). Contrary to enhanced coagulation which mainly removes only the HMW hydrophobic fraction of DOC, MIEX resins effectively remove both the hydrophobic HMW and hydrophilic LMW fractions of DOC (10). Water treatment with MIEX has been found to remove a wider range of molecular weights and organic acids of DOC than coagulation (16).

2.4.4 Ozonation

Ozonation is often used in combination with other treatment processes for NOM removal. It is used prior to granular activated carbon (GAC) filters in order to degrade recalcitrant organic matter and promote biodegradation of the more biodegradable organic carbon (11). However, when these fractions are not effectively removed in biofilters or adsorbed on GAC, they tend to be more difficult to remove due to their mobility and generally increased polarity (9). The ability of NOM to adsorb is known to decrease with ozonation because of the hydrophilic nature of the compounds.

The extent to which NOM is reduced in ozone enhanced biofiltration depends on several factors such as the applied ozone dose, characteristics of the NOM in the water and other water quality parameters like pH and alkalinity (16). Ozone changes the aromatic fraction of NOM, thus reducing the SUVA of the water. For NOM removal with ozone enhanced biofiltration, the ozone dose should be optimised. Particularly, ozone doses of 0.5 to 1.0 mg O_3/mg C are commonly applied prior to biofiltration (19). Ozonation of waters

containing bromide leads to formation of bromate, a DBP and potential carcinogen, which is not removed by subsequent biofiltration.

2.4.5 Membrane filtration

Membrane filtration systems such as ultrafiltration and nanofiltration can be used to remove larger organic matter and some dissolved NOM components left after coagulation. Ultrafiltration may be used to effectively remove larger MW organic compounds but it cannot remove lower MW organic matter < 100 Da. Nanofiltration membranes which have a lower MW cut off < 50 Da could be effectively used for the removal of NOM fractions which cannot be removed by ultrafiltration (12).

2.4.6 Bank filtration

Bank filtration (BF) systems have been used for the pre-treatment or complete treatment of river and lake waters to produce potable water. BF can remove particles, bacteria, viruses, parasites, organic compounds and potentially, nitrogen species (1). BF is known to effectively remove bulk NOM and some organic micropollutants (6). BF can achieve 50 to 90% reduction of biodegradable NOM (measured as biodegradable dissolved organic carbon (BDOC) and AOC) and 26% reduction in SUVA values for UV absorbing NOM (4).

2.4.7 Combined treatment processes and hybrids

Different combinations of removal methods have been employed for removal of NOM in drinking water. The main objective of these combined systems is to maximise the removal of specific fractions of NOM. These combined treatment systems may include (a) coagulation followed by ultrafiltration, (b) ozonation followed by activated carbon filtration, (c) activated carbon filtration followed by reverse osmosis, (d) biofiltration

followed by nanofiltration, (e) ion exchange followed by activated carbon filtration and (f) ozonation followed by biofiltration and membrane filtration (7; 18), which are found to be very effective when combined, and can remove up to 85% of dissolved NOM.

3. RESEARCH METHODS

3.1 Research design

Qualitative and quantitative approaches were used in this research. Different analytical parameters such as TOC, DOC, SUVA, SEC in combination with UV and fluorescence spectrometry were used for the determination of NOM in water samples.

3.1.1 Chemicals and materials

Sodium acetate

Milli-Q Water

Polystyrene sulphonate

0.45 mm acetate membrane.

pH Metter

Magnetic stirrer

Weighing balance

Measuring cylinder (500 mL)

Beakers (10, 100, 500 mL)

Vacuum pump

Buchner flask (100 ml)

Buchner funnel

0.45 μm cellulose acetate membrane (diameter)

HPSEC system consisting of a HPLC pump (Agilent 1200) Diode Array Detector

Fluorescence detector (Agilent 100 Series),

Agilent ChemStation for LC 3D Rev. A.10.02 Software

Agilent ProSec 300s silica column (7.5 mm × 300 mm, 10 μm)

3.2 Procedures

3.2.1 Sample collection and preparation

Water samples were collected at different points (shown in **Figure 3.1**) in the treatment plant process starting with the raw ponds (which is the final water from Gammams water care works) until the final flow point (which is after the ultrafiltration step at the WINGOC plant) in order to monitor how the NOM are distributed throughout the treatment plant. It should be noted that the samples were collected after each treatment was completed. Eight samples were collected once every week over a period of twelve months from January to December 2018. Samples were collected at each site in pre-cleaned 1000 mL Duran Schott glass bottles. Samples for the DOC and UV_{254} tests were filtered with 0.45 µm (Cole-Parmer® Nylon filter membranes) while the SEC samples were filtered with glass microfiber filters (47 mm) upon arrival at the laboratory, and the filtrate was analysed immediately after filtering. In cases where the DOC samples were not analysed immediately, they were preserved with 0.1 mL of phosphoric acid per 100 mL and stored in the refrigerator at 4°C and analysed within 3 days.

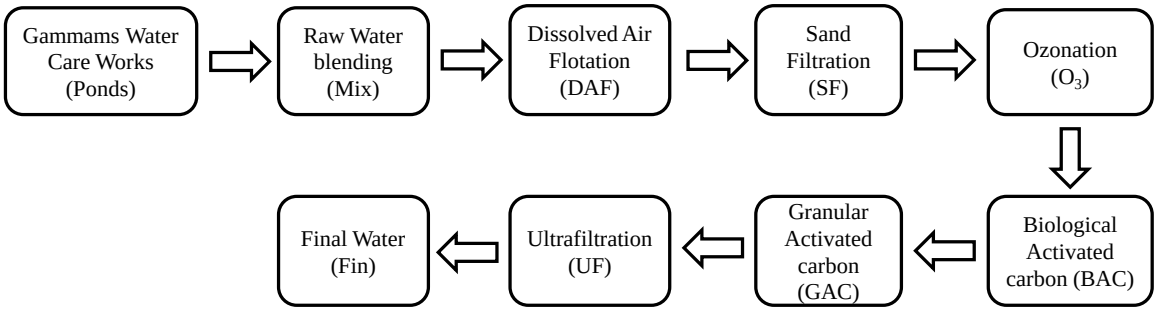


Figure 3.1 Different stages of the process train of the WINGOC treatment plant.

3.2.2 DOC, UV_{254} and SUVA measurements

The DOC contents of all pre-filtered samples were determined by the catalytic combustion method using a Fusion TOC-DOC organic carbon analyser on the day of sampling. In the TOC-DOC organic carbon analyser, the inorganic carbon was removed first by acidification and spurging and the organics were then oxidised into carbon dioxide (CO_2) by persulphate in the presence of UV-light and measured as DOC after. Samples were filtered through a 0.45 μm filter into a clean 50 mL headspace vials and the vials were tightly capped (17). UV absorbance at 254 nm (UV_{254}) of each sample was measured at room temperature (20 °C) using a Specord 210 plus spectrophotometer. Subsequently, SUVA values were calculated using **equation 2.1**. DOC samples were analysed together with calibration standards with a correlation coefficient, $R^2 > 0.998$ using certified reference materials. Averages and standard deviations were calculated at each treatment stage for each month.

3.2.3 Nutrients (Nitrates) measurements

Nitrate was determined spectrophotometrically after reduction of nitrates to nitrite by cadmium copper. The sample was buffered at pH 8.2 and then passed through the column containing copper-cadmium to reduce nitrate to nitrite. The nitrite which was originally present plus the reduced nitrates was then determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)ethylenediamine dihydrochloride to form a highly coloured azo dye which was measured at 540 nm (17).

3.2.4 Temperature and pH

Temperature and pH were measured using the Mettler Toledo multimeter. The probes were calibrated using standard buffer solutions before measurements were taken.

3.2.5 Size exclusion chromatography with UV and FLD detection

The molecular weight distribution of the organic fractions was determined using high pressure size exclusion chromatography (HPSEC or SEC). Analyses were performed on an Agilent 1260 liquid chromatograph equipped with a quaternary pump, autosampler, column oven, fluorescence and UV/Vis detectors. Analyses were performed on an Agilent ProSec 300s silica column (7.5 mm × 300 mm, 10 μm). The pH of the samples were adjusted to 7 and passed through a 0.45 μm filter membrane (GE Water & Process Technologies) before injection. A flow rate of 1.00 mL/min and an injection volume of 300 μL were used. A mobile phase of 0.5 M aqueous sodium acetate was used. A total run time of 15 min was used (18). UV detection was performed at 210 and 254 nm. Spectral UV data were also recorded between 200 and 700 nm. For fluorescence detection (FLD), the excitation wavelength was set at 230 nm and the emission wavelength was set at 460 nm, while spectral fluorescence data were recorded between 220 and 300 nm (excitation wavelengths) and 280-400 nm (emission wavelengths). The molecular weight of organics was determined by size calibration using four sodium polystyrene sulfonate standards (Scientific Polymer Products Inc) with molecular weights of 210, 4 200, 6 800 and 10 000 Da. Data acquisition and processing was performed using the Agilent Chemstation software version 8.

3.3 Research ethics

Permission was obtained from WINGOC to use their facilities, including the use of their sampling equipments when needed. Research ethical clearance was obtained from the University of Namibia's Research Ethics Committee (UREC) (see **Appendix 2**). Research permission was obtained from the University of Namibia's Centre for

Postgraduate Studies. All waste generated in the laboratory was disposed off according to the guidelines for waste disposal in the department.

4. RESULTS AND DISCUSSION

4.1 Determination of the DOC, UV_{254} absorbance, NO_3 and SUVA

The organic content of the water samples was measured in terms of DOC, which gives an indication on the type of NOMs that are present. The results for the DOC contents of the water samples collected at different treatment stages throughout the plant are shown in **Figure 4.1 (**see **Appendix 1.1** for the raw data). As expected, the DOC content was higher in the raw water and mixing ponds, with DOC values in excess of 4.5 mg/L for all the months, and decreased gradually as the water is passing through the different treatment stages. Careful study of the DOC data reveals that very high DOC removal efficiencies were achieved, with removal percentage of up to 98% noted for some months.

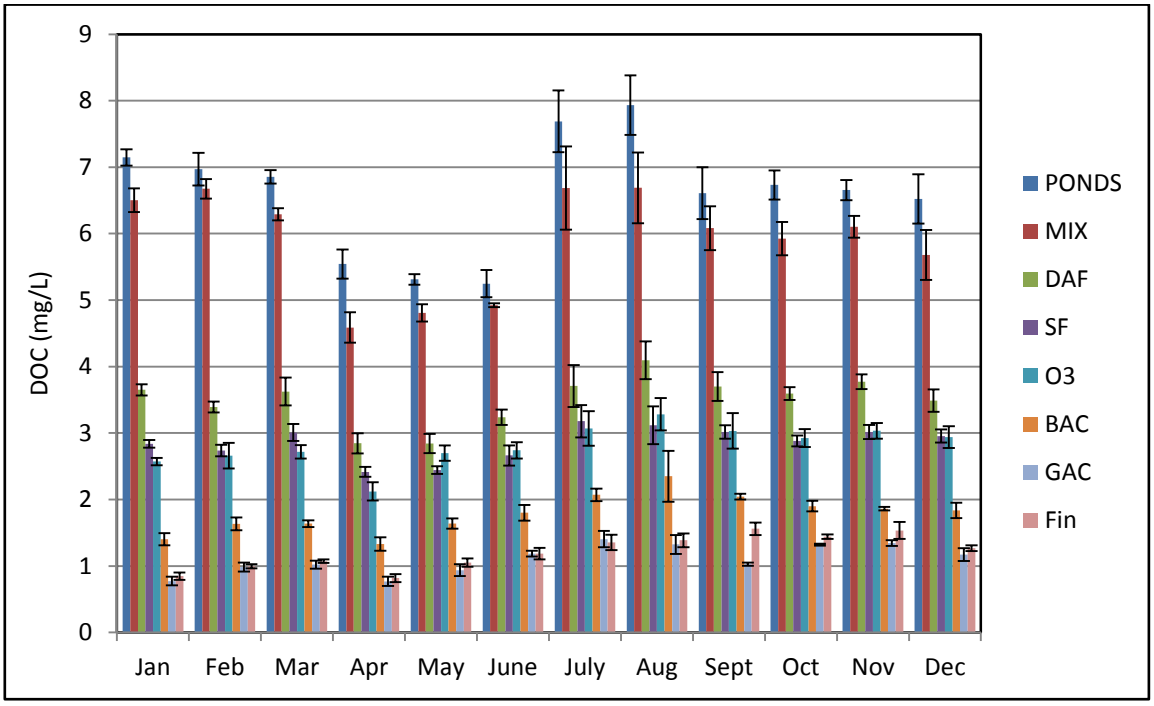
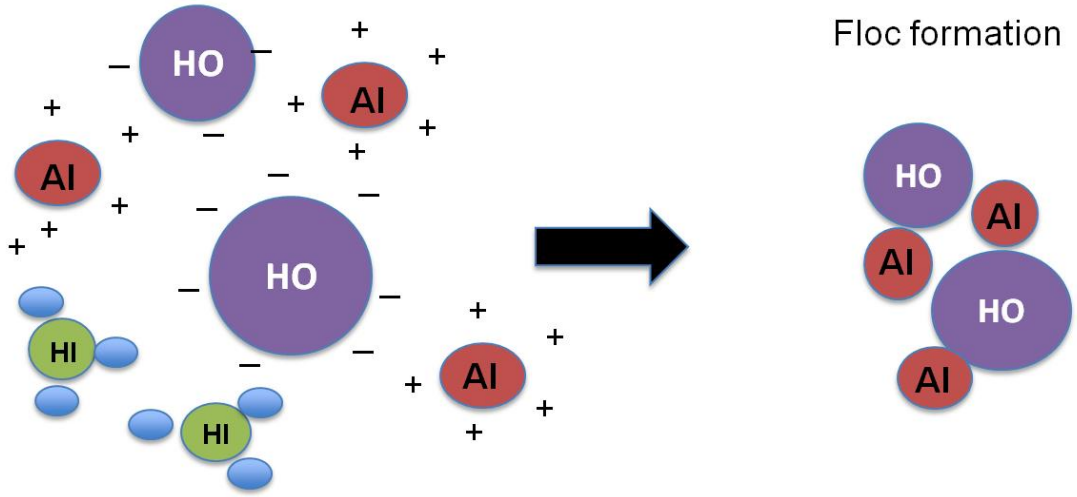


Figure 4.1: DOC data (average ± standard deviation) for the water samples collected at different treatment stages at WINGOC treatment plant from January to December 2018.

When comparing the DOC contents measured at different treatment stages, it is seen that the DOC contents decreased drastically after the DAF (38-49%), BAC (28-45%) and GAC (27-50%) treatment steps. The DAF process facilitates removal of suspended matter (some of which could be organic matter) from the water through the use of dissolved air, which causes suspended matter to float on top or settle to the bottom, where they can easily be removed (1; 18), therefore this observation is consistent with theory (5). A significant reduction in DOC at the BAC stage is also expected since BAC is preceded by ozonation which converts HMW organic matter to smaller biodegradable organic molecules, which then expedite removal of organics through physical adsorption and biodegradation processes (18; 19). DOC removal at the sand filtration stage was in the range of 14-24%. Limited DOC removal (< 13%) was noted at the ozonation stage, which could indicate that oxidation led to the formation of transformation products rather than mineralisation (19). While organic matter may be converted to more biodegradable organics through ozonation, there is nothing to speed up this degradation process (e.g. degradation catalyst), therefore the small reduction in DOC is not surprising (18). These observations are consistent with literature reports (6).

Although all treatment methods were able to reduce the DOC content of the water, albeit to different extents, none of the methods applied could remove the dissolved organic matter completely. According to the World Health Organisation (WHO), the maximum allowable DOC for drinking water is 5 mg/L. Therefore, it can be said that the treatment process as a whole is effective in the reduction of the organic matter since the DOC contents were all less than 1.6 mg/L in the final water which indicates the suitability of water for general use.

UV absorbance data at 254 nm are shown in **Figure 4.3** (raw data in **Appendix 1.2**). The UV_{254} measurements show a gradual reduction in UV absorbance as the water is passing through the different treatment stages, with the most significant reduction (41-59%) observed after the ozonation stage. This reduction in UV absorbance could be ascribed to the loss of aromaticity due to depolymerisation of HMW organic matter, as is normally observed in samples of natural waters containing high levels of humic substances (15) as exemplified in **Figure 4.2** below.



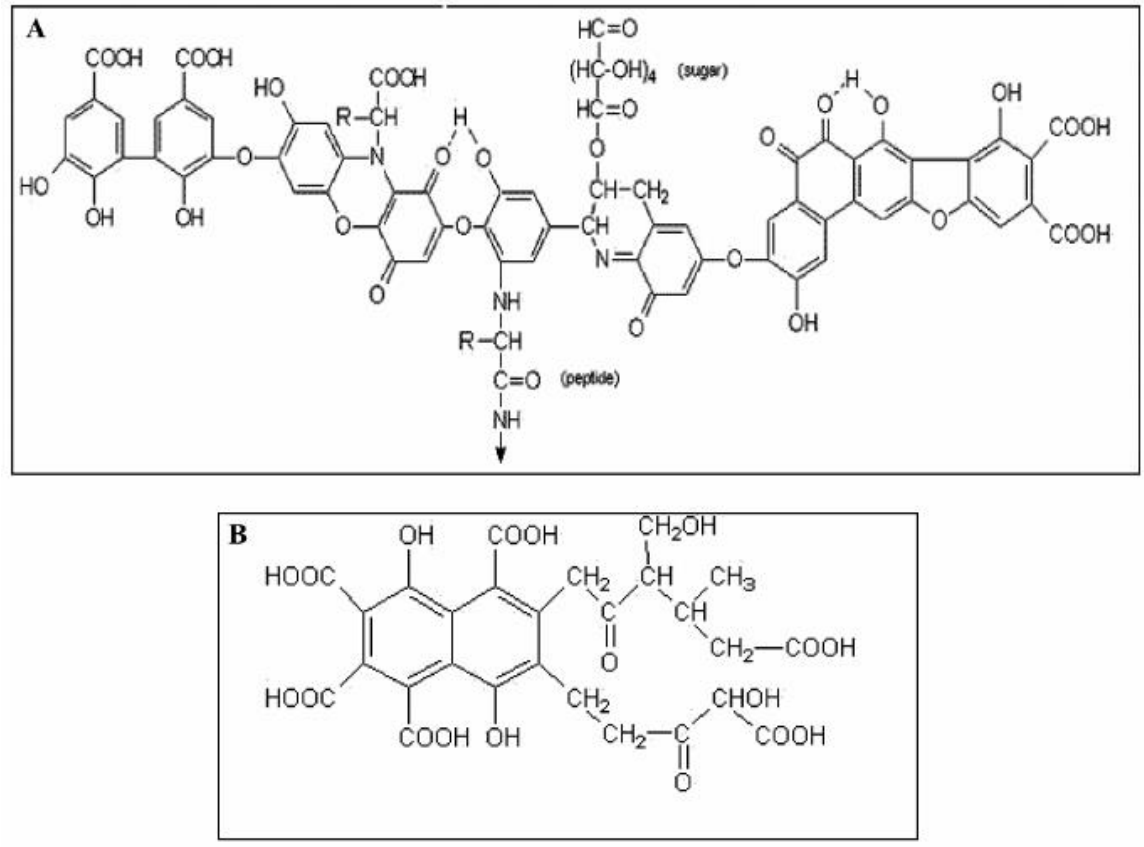


Figure 4.2 Depolymerisation of HMW (A) to LMW (B) structure (16) .

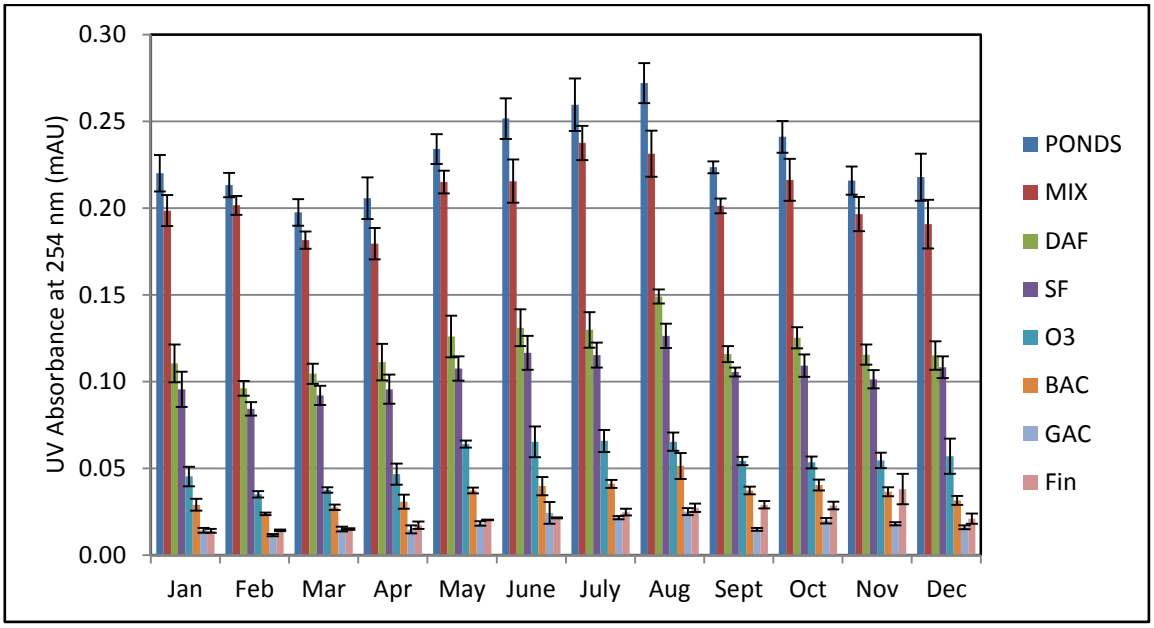


Figure 4.3: UV_{254} data for the water samples collected at different treatment stages at WINGOC treatment plant from January to December 2018.

Water samples collected at treatment stages before ozonation were characterised by SUVA values ranging between 2.88 and 4.80 $Lmg^{-1}m^{-1}$, while these values were below 2.38 $Lmg^{-1}m^{-1}$for treatment stages after ozonation (**Figure 4.4**). In general, SUVA could be utilised to provide the relative index of the humic content of the DOC in water [6]. Natural waters with high SUVA values, i.e. ≥ 4.00 $Lmg^{-1}m^{-1}$ have a relatively high content of hydrophobic, aromatic and high molecular weight NOM fractions, whereas waters with SUVA of ≤ 2 $Lmg^{-1}m^{-1}$ largely contain non-humic, hydrophilic and low molecular weight substances (**Table 2.1**). Using this guide, it can then be hypothesised that the NOM fractions at the WINGOC treatment plant contained complex mixtures of humic- and non-humic substances with varying sizes and degrees of hydrophobicity/aromaticity as can be deduced from the high UV absorbance and SUVA data obtained for the treatment stages before ozonation, and these were converted to hydrophilic, low molecular weight organics with low UV absorbance and SUVA values after the ozonation process. No clear trends could be discerned with regard to seasonal variations.

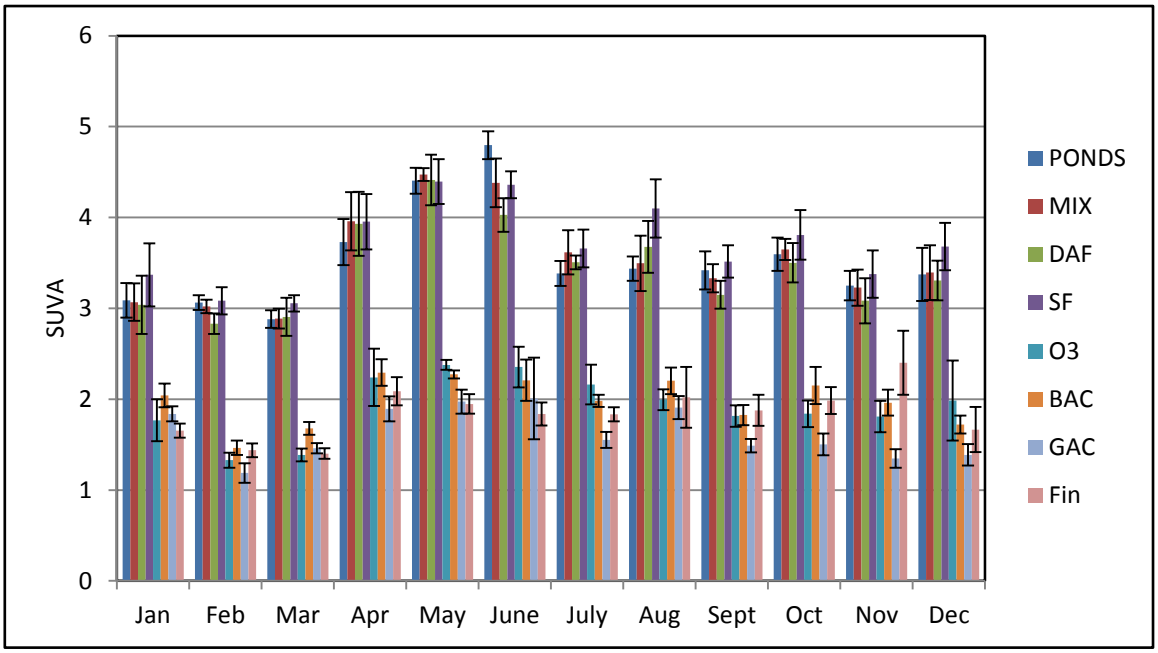


Figure 4.4: SUVA data for the water samples collected at different treatment stages at WINGOC treatment plant from January to December 2018 (see **Appendix 1.3** for raw data).

From the nutrients (nitrates) data presented in **Figure 4.5**, it can be seen that the nitrates levels remained constant throughout the treatment process (from Ponds to Final). This is due to the fact that nitrates are removed at the secondary treatment stage (at the Gammams wastewater treatment plant) and there are no measures in place for further removal of nitrates at the tertiary treatment stage. It is worth mentioning that the nitrate values were all below 16 mg/L, which is the maximum allowable limit for drinking water according to the WHO. This indicates that the Gammams wastewater treatment plant is effective in removing these compounds, therefore there is no need for further removal of nitrates at the WINGOC treatment plant.

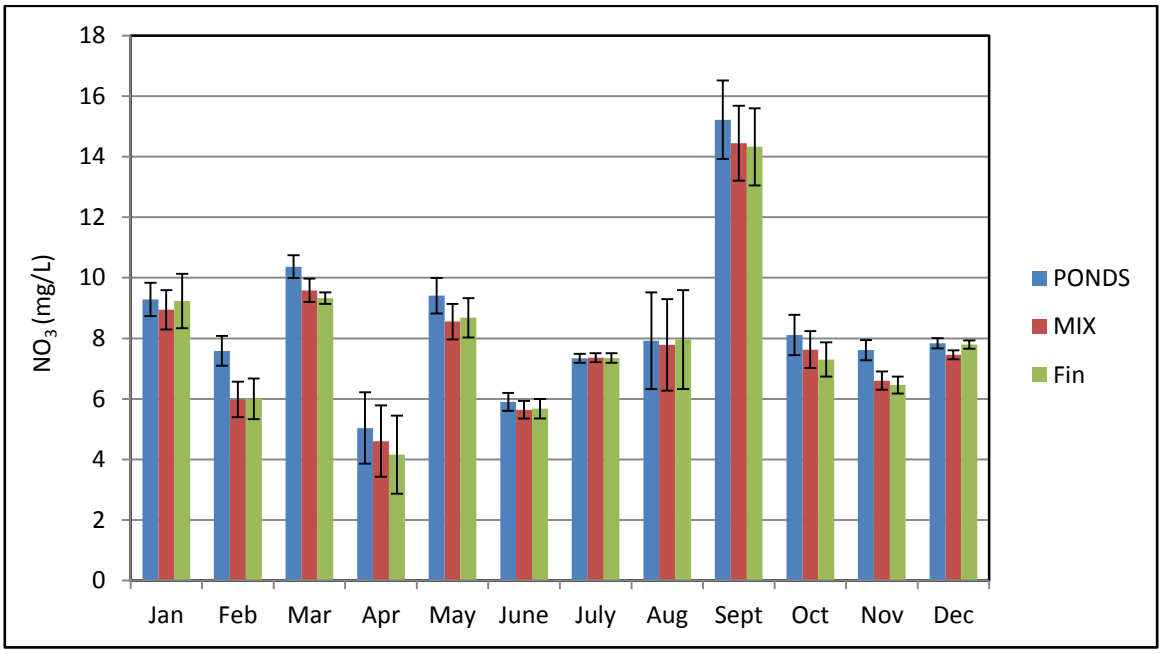


Figure 4.5: Average NO_3^- data for the water samples collected at three treatment stages (Ponds, Mix and Final) at WINGOC treatment plant from January to December 2018

4.2 pH and temperature measurements

Temperature and pH are known to affect performance in water treatment plants, therefore these two parameters were also measured to determine if they had an effect on the removal of organic matter in water. pH and temperature data are shown in **Figures 4.6** and **4.7**, respectively. From the pH data (**Figure 4.6**), it can be noted that there is a slight reduction in the pH values for all the samples after ozonation, confirming the oxidation effect of ozone on the NOM and the generation of lower molecular weight substances which were probably acidic in nature (12). Furthermore, the pH shows an increase at the last step of the treatment process, which could be attributed to the addition of caustic soda (NaOH) which is added during the chemical stabilisation stage. No seasonal variations of pH were observed.

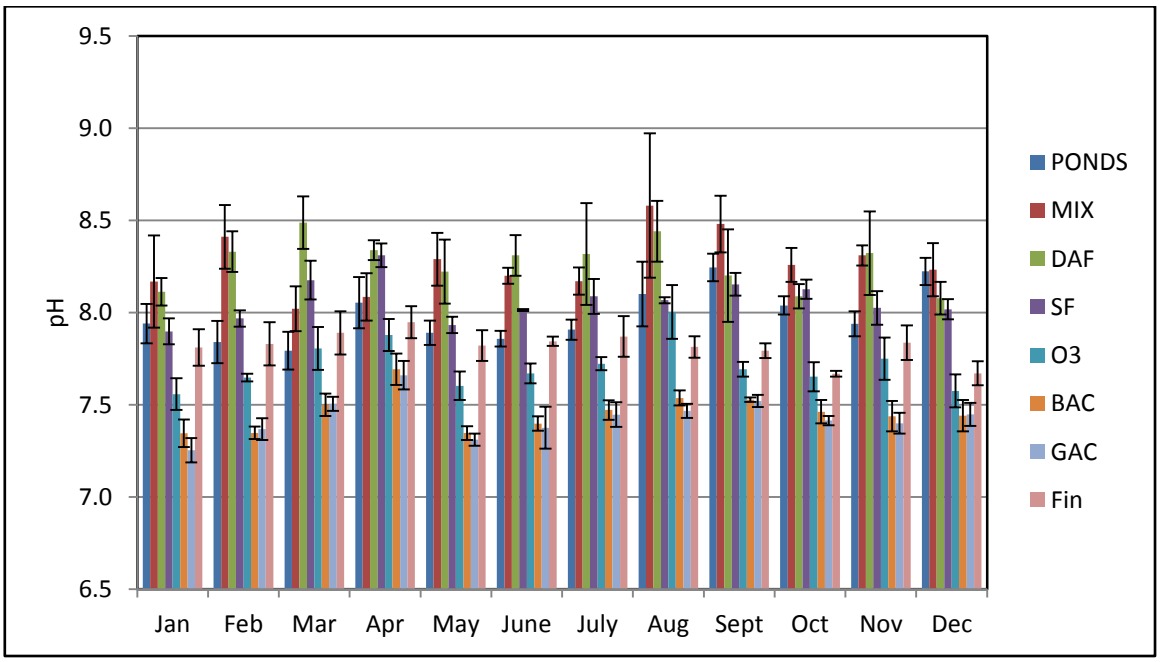


Figure 4.6: pH values for the water samples collected at different treatment stages at WINGOC treatment plant from January to December 2018 (see **Appendix 1.4** for raw data).

Temperature data presented in **Figure 4.7** (raw data in **Appendix 1.5**) show a slightly high temperature (> 20 °C) for earlier months of the year (January to April), a slight reduction in temperature (< 20 °C) in colder months (May to July) and a gradual increase as it got warmer again from August to December. It is interesting to note that the temperature was slightly higher for the ozonation and BAC stages for all the months, which could be an indication of the exothermic nature of reactions taking place at these stages.

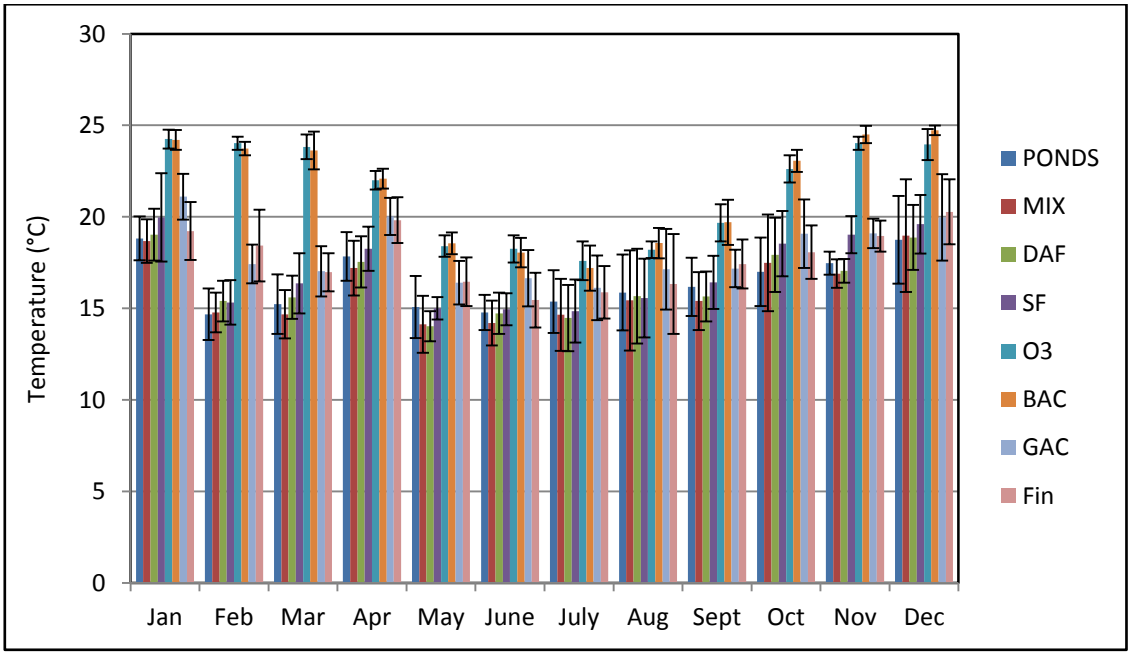


Figure 4.7: Temperature values for the water samples collected at different treatment stages at WINGOC treatment plant from January to December 2018.

4.3 HP-SEC-UV-fluorescence analysis

HP-SEC chromatograms for the standards and water samples before (Ponds) and after (Final) treatment for two representative months (July and October) are shown in **Figure 4.8**. As can be seen from **Figure 4.8A**, NOM present in water samples had molecular weights falling between 210 to 10000 g/mol. As previously discussed in **Section 4.1**, it is clearly illustrated how the UV absorbance was progressively decreasing as the water goes from the first to the last treatment stage. Both UV and fluorescence chromatograms revealed two peaks for the ponds and blended (mix) water and only one peak was observed in the water samples collected at other treatment stages. The first peak (**Peak 1**, highest molecular weight) which was detected at approximately 9 min in **Figure 4.9** and observed in raw and blended water, could belong to very HMW compounds (MW > 10 000 g/mol) such as polysaccharides, proteins and/or colloids. This peak is often associated with the presence of bacterial residual compounds in the water and is always present in surface water (1). High concentrations of polysaccharides, proteins and colloids peak are associated with high fouling rates on low pressure membranes (7).

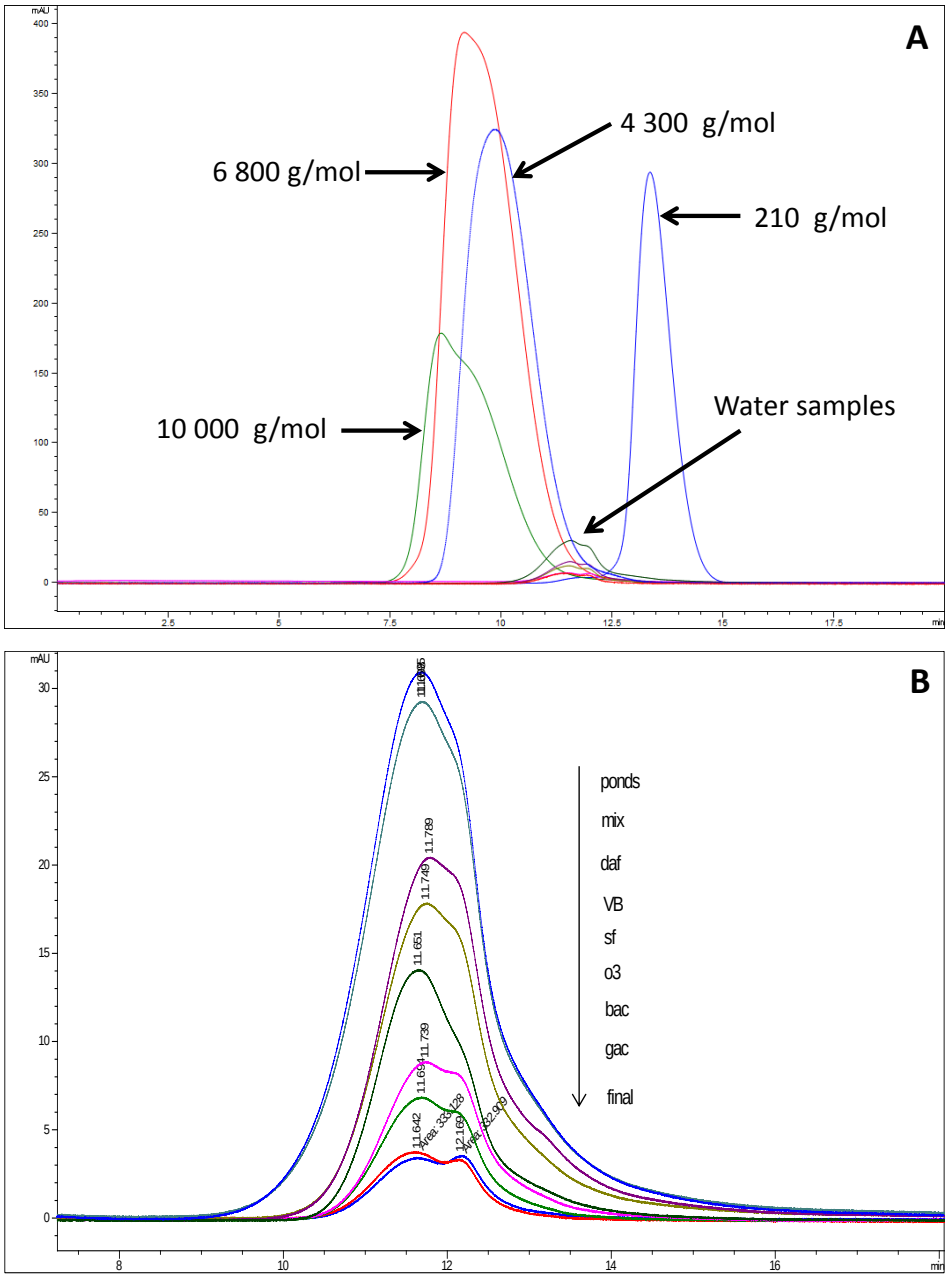


Figure 4.8: Chromatograms for differently sized polystyrene sulfonate standards overlaid with chromatograms for the water samples collected at different treatment stages at the WINGOC treatment plant in January 2018 (A) and chromatograms for the water samples only (B) measured at DAD 254 nm. VB represents a water sample obtained at the von Bach dam.

The second peak (**Peak 2)** around 12 min could be attributed to HMW aromatic organic molecules (MW between 210 – 10 000 Da) e.g. humic substances (HS) and the

corresponding building blocks. This fraction usually constitutes a large portion of organic matter in surface water, and represents 50 to 60% of the DOC (19). This fraction was present at all the treatment steps, although it is found to be low in GAC and final water.

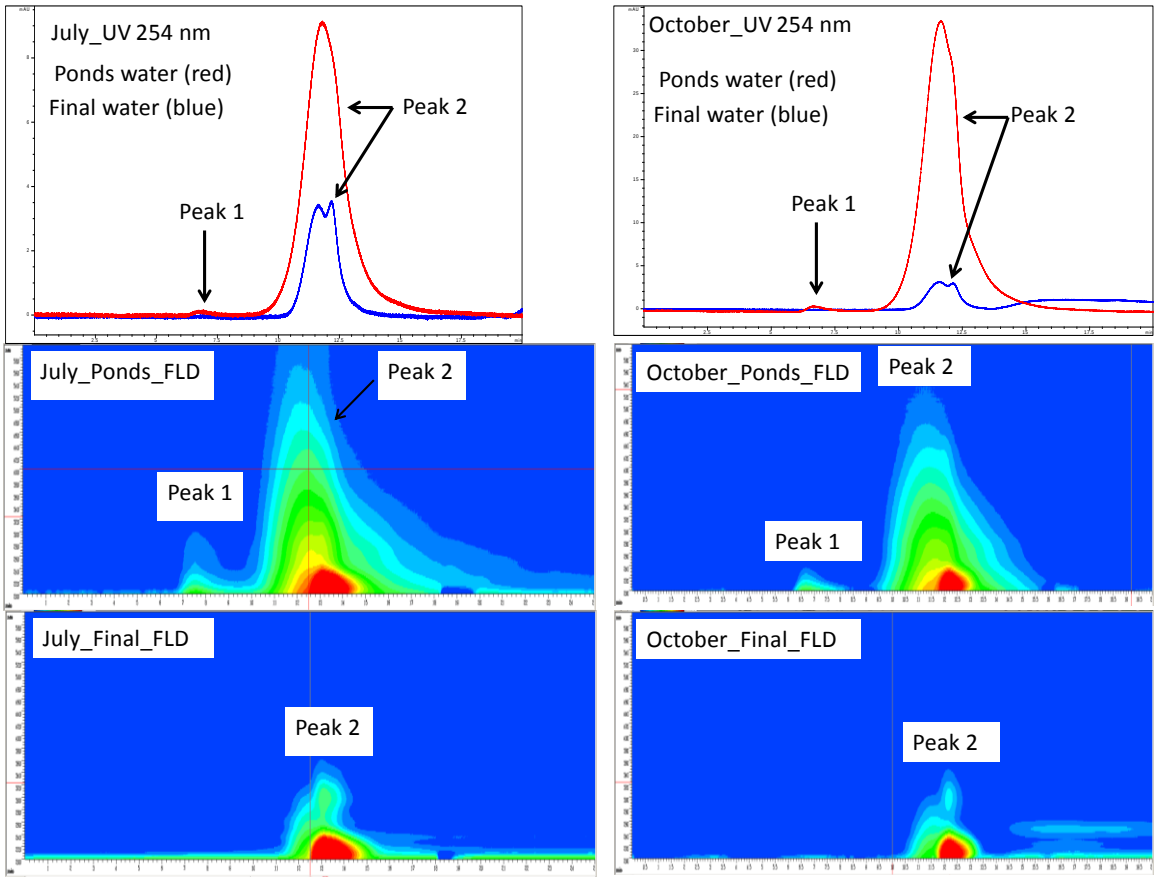


Figure 4.9: SEC-UV chromatograms at 254 nm (top) and corresponding fluorescence contour plots for ponds and final water samples for July and October 2018 (bottom).

The fluorescence data are shown in **Figure 4.9** which indicates the breakdown of NOM into smaller molecular weight compounds, resulted in the shift of the fluorescence from high spectra (Ponds) to shorter emission wavelengths Final water.. The investigation of the changes in the fluorescence peak locations was restricted to the humic-like peak 1, which has been shown to be abundant in aquatic NOM as well as raw water. The F-EEM spectra of WINGOC water Raw (Ponds) and after Ultrafiltration (Final) presented in

Figure 4.9 in the form of contour plots are showing a great shift and this was observed using the Chemstation software, which involved manually selecting the point of maximum intensity fluorescence intensity within the peak 1 region.

The molecular weight distribution data is well supported by the UV_{254} and SUVA results presented in **Section 4.1** earlier, and they are in agreement with the findings of other studies (10; 14). Unfortunately, the types of fluorophores present in the water samples could not be identified from the excitation-emission spectral data due to technical difficulties.

5. Conclusions and Recommendations

Water quality monitoring in Namibia still rely on general parameters such as DOC, pH, chemical oxygen demand, turbidity, etc., but less to no attention is given to NOM characterisation in treatment plants and drinking water. In this study, NOM in water samples from WINGOC treatment trains was characterised using multiple analytical tools including DOC, UV, SUVA, SEC and fluorescence spectroscopy.

Raw water was found to have a high organic content which gradually reduced as the water passes through different treatment stages. The DOC measurements were directly proportional to the UV absorbance and SUVA of the water samples. From the SUVA results it could be tentatively said that the raw water contained complex mixtures of high molecular weight humic- and non-humic substances with varying sizes and degrees of hydrophobicity/aromaticity. These results were further supported by the molecular weight distribution data obtained in size exclusion chromatography.

Although none of the treatment methods seem to remove the NOM fraction completely, it can be said that the WINGOC water treatment process as a whole is effective in removing organic matter as the final water contained DOC levels that are well within the acceptable limits for drinking water. Seeing that DOC analysis can only give a clue on the amount of NOM present in a sample but not give any insight into the structure and character of the NOM, it is therefore highly recommended that further characterisation of the NOM be conducted using other techniques that may provide the detailed chemical composition of the NOM. High performance size exclusion chromatography coupled with UV-Vis, fluorescence, light scattering, mass spectrometry and sensitive dissolved organic carbon detection techniques could be used to obtain information on molecular

absorbance, size distribution, molar mass and NOM reactivity. It is further recommended that the study be conducted over a longer period of time to allow evaluation of the effect of seasonal variations on the organic content of the water as this was not very clear in the current study.

6. References

1. Haarhoff, J. *Natural Matter in Dinking Water Sorces: Its Characterization and Treatability.* Johannesburg : Water Research Commission, 2013.

2. Lempert, J. Lahnsteiner & G.*Water Management in Windhoek, Namibia.* Water Science & Technology, 2007, pp. 441-448.

3. Merwe, J. Haarhoff & B. Van der. *Twenty five years of waste water reclamation in Windhoek, Namibia.* Water Science and Technology,1996, pp. 25-35.

4. Brazrafshan, Edris, Biglari, Hamed and Mostatafapour, Ferdos Kord. *Determinarion of Hydrophobic and Hydrophillic Fractions of Natural Organic matter in Raw Water of Zahedan Water Treatment Plant.* 2012, Health Scope, pp. 25-28.

5. Menge, B. VAn der Merwe & J. *Water reclamation for the portable reuse in Windhoek, Namibia.* Sydney : s.n., 1996. Water Tech Conference. pp. 327-333.

6. J. Reungoat, B.I. Escher , M. Macova , F.X. Argaud , W. Gernjak , J. Keller.*Ozonation and biological activated carbon filtration of wastewater treatment plant effluents.* 2012, Water Research, Vol. 46, pp. 863 -872.

7. Cui, Xiaojun and Choo, Kwang-Ho.*Natural Organic Matter Removal and Fouling Control in Low-Pressure Membrane Filtration for Water Treatment.* 2014, Environment Engineering Research, pp. 1-8.

8. Cunha, Claudia Isabel Martins Paiva e. *Natural Organic Matter Characterization in Drinking Water by Fluorescence Spectroscopy.* Lisboa : s.n., 2014.

9. Swietliek, J and Sikorska, E.*Characterization of Natural Organic Matter Fractions by High Pessure Size-Exclusion Chromatography, Specific UV Absorbance and Total Luminescence Spectroscopy.* 2005, Polish Journal of environmental Studies, pp. 145-153.

10. Haarhoff, J, et al. *NOM characterization and removal at six southern African water treatment plants.* 2010, Drinking Water Engineering and Science, pp. 53-61.

11. Ibrahim, Nurazim and Aziz, Hamidi Abdul. *Trends on Natural Organic Matter in Drinking Water Sources and its Treatment.* 2014, International Journal of Scientific Research in Environmental Sciences, pp. 94-106.

12. Montreuil, Krysta Rose. *Natural Organic Matter Characerization in Drinking Water.* Nova Scotia : Dalhousie University , 2011.

13. O'Driscoll, Connie, et al. *Assesment of Natural Organic Matter (NOM) and Ptaquiloside in Irish Waters.* Johnstown Castle : Environmental Protection Agency, 2017.

14. Her, Namguk, et al.*Optimization of Method for Deteting and Characterizing NOM by HPLC-Size Exclusion Chromatography with UV and On-Line DOC Detection.* 20021069-1076, Environmental Science and Technology.

15. Ji-Eun Lee, Byung-Suk Jin, Sung-Hoon Cho, Sung-Hwan Han, Oh-Shim Joo and Kwang-Deog Jung. *Catalytic Ozonation of Humic Acids with Fe/MgO]*. 4, 2005, Korean J.Chem. Eng., Vol. 22, pp. 536-540.

16. Vasyukova, EKATERINA, et al.*Removal of Natural Organic Matter and Trihalomethane formation potential in a full-scale water treatment plant.* 2013, Water Science and Technology: Water Supply, pp. 1100-1107.

17. APPHA. *Standard Method for examination of water and waste water.* 2005.

18. Sillanpaa, Mika. *Natural Organic Matter in Water: Characterization and Treatment Methods* . Oxford : Elsevier, 2015.

19. J. Reungoat, B.I. Escher, M. Macova, F.X. Argaud, W. Gernjak, J. Keller. *Ozonation and biological activated carbon filtration of wastewater treatment plant effluents* . 2012, Water Research, Vol. 46, pp. 863 -872).

20. Tao, Hengfeng Miao and Wenyi.*Ozonation of humic acid in water.* 2008, J Chem Technol Biotechnol, Vol. 83, pp. 336-344.

Appendices

Appendix 1 Raw data for different parameters as measured at different treatment stages at WINGOC treatment plant for the year 2018.

Appendix 1.1 Average monthly DOC data at different treatment stages at WINGOC treatment plant for the year 2018.

Treatment Stages	**Average monthly DOC readings (mg/L)**											
	Jan	**Feb**	**March**	**April**	**May**	**June**	**July**	**Aug**	**Sept**	**Oct**	**Nov**	**Dec**
PONDS	7.15±0.25	6.97±0.49	6.86±0.20	5.54±0.49	5.31±0.16	5.25±0.41	7.69±0.93	7.93±0.77	6.61±0.78	6.73±0.49	6.66±0.30	6.52±0.74
MIX	6.50±0.35	6.68±0.29	6.29±0.18	4.59±0.51	4.81±0.26	4.92±0.06	6.69±1.25	6.69±0.92	6.08±0.66	5.93±0.56	6.11±0.33	5.68±0.75
DAF	3.65±0.17	3.39±0.17	3.63±0.42	2.85±0.34	2.84±0.29	3.24±0.23	3.71±0.63	4.09±0.49	3.70±0.43	3.59±0.22	3.77±0.22	3.49±0.34
SF	2.84±0.12	2.74±0.18	3.01±0.25	2.42±0.16	2.44±0.12	2.66±0.30	3.18±0.40	3.12±0.49	3.02±0.20	2.88±0.18	3.02±0.21	2.96±0.20
O_3	2.57±0.11	2.66±0.38	2.72±0.21	2.12±0.30	2.70±0.23	2.74±0.25	3.07±0.52	3.28±0.42	3.03±0.53	2.93±0.30	3.04±0.24	2.94±0.33
BAC	1.41±0.18	1.64±0.19	1.64±0.10	1.33±0.23	1.64±0.15	1.80±0.23	2.07±0.19	2.35±0.66	2.04±0.09	1.90±0.18	1.86±0.06	1.84±0.23
GAC	0.77±0.13	0.98±0.14	1.02±0.12	0.77±0.15	0.94±0.18	1.19±0.09	1.41±0.24	1.32±0.25	1.03±0.04	1.32±0.03	1.35±0.09	1.17±0.19
Fin	0.85±0.11	1.00±0.06	1.07±0.05	0.82±0.13	1.05±0.13	1.19±0.17	1.36±0.23	1.39±0.18	1.56±0.19	1.44±0.08	1.54±0.25	1.27±0.08

Appendix 1.2 Average monthly UV_{254} data at different treatment stages at WINGOC treatment plant for the year 2018.

Treatment Stages	**Average monthly UV_{254} readings (mAU)**											
	Jan	**Feb**	**March**	**April**	**May**	**June**	**July**	**August**	**Sept**	**Oct**	**Nov**	**Dec**
PONDS	0.220±0.021	0.213±0.014	0.198±0.015	0.206±0.027	0.234±0.017	0.252±0.023	0.260±0.927	0.272±0.020	0.224±0.007	0.241±0.021	0.216±0.016	0.218±0.027
MIX	0.199±0.018	0.202±0.011	0.182±0.010	0.179±0.020	0.215±0.013	0.216±0.025	0.238±1.253	0.231±0.023	0.201±0.008	0.216±0.027	0.197±0.020	0.191±0.028
DAF	0.111±0.022	0.096±0.009	0.105±0.012	0.111±0.023	0.126±0.024	0.131±0.021	0.130±0.627	0.149±0.007	0.116±0.009	0.125±0.013	0.116±0.012	0.115±0.016
SF	0.096±0.020	0.084±0.008	0.092±0.011	0.096±0.019	0.108±0.014	0.117±0.020	0.115±0.487	0.126±0.012	0.106±0.005	0.109±0.014	0.101±0.011	0.108±0.012
O_3	0.045±0.011	0.035±0.004	0.038±0.003	0.047±0.013	0.064±0.004	0.065±0.018	0.066±0.521	0.065±0.009	0.054±0.005	0.053±0.008	0.055±0.009	0.057±0.020
BAC	0.029±0.007	0.024±0.002	0.028±0.003	0.031±0.009	0.037±0.003	0.040±0.010	0.041±0.187	0.051±0.013	0.037±0.004	0.040±0.007	0.037±0.005	0.032±0.005
GAC	0.014±0.003	0.012±0.001	0.015±0.003	0.015±0.005	0.018±0.003	0.024±0.013	0.022±0.244	0.025±0.003	0.015±0.002	0.020±0.003	0.018±0.002	0.016±0.002
Fin	0.014±0.002	0.014±0.001	0.015±0.001	0.017±0.005	0.020±0.001	0.022±0.001	0.025±0.228	0.027±0.004	0.029±0.004	0.029±0.005	0.038±0.017	0.021±0.006

Appendix 1.3 Average monthly SUVA data at different treatment stages at WINGOC treatment plant for the year 2018.

Treatment Stages	Average monthly SUVA readings ($Lmg^{-1}m^{-1}$)											
	Jan	**Feb**	**March**	**April**	**May**	**June**	**July**	**August**	**Sept**	**Oct**	**Nov**	**Dec**
PONDS	3.09±0.38	3.06±0.16	2.88±0.19	3.73±0.57	4.40±0.29	4.80±0.31	3.38±0.27	3.44±0.23	3.42±0.42	3.60±0.41	3.25±0.32	3.37±0.59
MIX	3.07±0.41	3.02±0.15	2.89±0.22	3.96±0.72	4.47±0.14	4.38±0.53	3.62±0.48	3.50±0.53	3.33±0.31	3.65±0.26	3.23±0.40	3.39±0.60
DAF	3.04±0.64	2.83±0.22	2.91±0.42	3.93±0.78	4.41±0.56	4.03±0.37	3.51±0.15	3.68±0.49	3.15±0.31	3.50±0.49	3.08±0.50	3.31±0.44
SF	3.37±0.69	3.08±0.30	3.05±0.18	3.95±0.68	4.40±0.49	4.36±0.30	3.66±0.42	4.10±0.55	3.52±0.36	3.81±0.61	3.38±0.52	3.68±0.52
O_3	1.77±0.46	1.33±0.16	1.39±0.14	2.24±0.70	2.38±0.11	2.35±0.45	2.16±0.43	1.99±0.20	1.82±0.24	1.84±0.33	1.81±0.34	1.99±0.88
BAC	2.04±0.26	1.46±0.16	1.68±0.14	2.29±0.33	2.27±0.09	2.21±0.46	1.98±0.13	2.20±0.25	1.83±0.22	2.15±0.46	1.96±0.29	1.72±0.20
GAC	1.84±0.16	1.19±0.22	1.46±0.11	1.89±0.31	1.97±0.27	2.01±0.90	1.55±0.18	1.91±0.22	1.49±0.15	1.50±0.27	1.35±0.21	1.39±0.24
Fin	1.65±0.15	1.44±0.15	1.40±0.12	2.09±0.35	1.95±0.22	1.84±0.25	1.83±0.16	2.02±0.58	1.88±0.34	1.99±0.33	2.40±0.71	1.67±0.50

Appendix 1.4 Average monthly pH data at different treatment stages at WINGOC treatment plant for the year 2018.

Treatment Stages	Average monthly pH readings											
	Jan	**Feb**	**March**	**April**	**May**	**June**	**July**	**August**	**Sept**	**Oct**	**Nov**	**Dec**
PONDS	7.94±0.21	7.84±0.23	7.79±0.20	8.05±0.31	7.89±0.13	7.86±0.08	7.91±0.11	8.10±0.30	8.25±0.15	8.04±0.11	7.94±0.14	8.22±0.15
MIX	8.17±0.50	8.41±0.35	8.02±0.24	8.08±0.29	8.29±0.29	8.20±0.09	8.17±0.15	8.58±0.68	8.48±0.31	8.26±0.21	8.31±0.11	8.23±0.29
DAF	8.11±0.15	8.33±0.22	8.49±0.28	8.34±0.12	8.22±0.35	8.31±0.22	8.32±0.55	8.44±0.29	8.20±0.50	8.09±0.15	8.32±0.45	8.08±0.18
SF	7.90±0.14	7.97±0.09	8.18±0.21	8.31±0.14	7.93±0.09	8.01±0.01	8.09±0.19	8.07±0.03	8.15±0.12	8.13±0.12	8.03±0.18	8.02±0.11
O3	7.56±0.17	7.65±0.04	7.81±0.23	7.88±0.19	7.60±0.15	7.67±0.11	7.72±0.07	8.00±0.25	7.69±0.08	7.65±0.18	7.75±0.23	7.58±0.18
BAC	7.35±0.15	7.35±0.07	7.50±0.12	7.69±0.19	7.35±0.07	7.40±0.08	7.47±0.11	7.54±0.07	7.53±0.02	7.46±0.14	7.44±0.16	7.44±0.17
GAC	7.25±0.13	7.37±0.12	7.51±0.08	7.66±0.17	7.31±0.07	7.38±0.23	7.45±0.13	7.47±0.07	7.52±0.07	7.41±0.06	7.40±0.11	7.45±0.13
Fin	7.81±0.20	7.83±0.23	7.89±0.23	7.95±0.19	7.82±0.17	7.84±0.05	7.87±0.22	7.81±0.10	7.79±0.08	7.67±0.04	7.84±0.19	7.67±0.13

Appendix 1.5 Average monthly temperature data at different treatment stages at WINGOC treatment plant for the year 2018.

Treatment Stages	Average monthly temperature readings (°C)											
	Jan	**Feb**	**March**	**April**	**May**	**June**	**July**	**August**	**Sept**	**Oct**	**Nov**	**Dec**
PONDS	18.8±2.4	14.7±2.8	15.2±3.3	17.8±3.0	15.1±3.4	14.8±1.9	15.4±3.4	15.9±3.6	16.2±3.2	17.0±4.2	17.5±1.3	18.8±4.8
MIX	18.7±2.4	14.8±2.2	14.7±2.6	17.2±3.3	14.1±3.1	14.2±2.5	14.7±3.9	15.4±4.73	15.4±3.2	17.5±5.9	16.9±1.5	19.0±6.1
DAF	19.0±2.8	15.4±2.2	15.6±2.4	17.5±3.1	14.0±1.7	14.7±2.3	14.5±3.6	15.7±4.5	15.7±2.7	17.9±4.5	17.1±1.3	18.9±3.6
SF	20.0±4.8	15.3±2.4	16.4±3.3	18.3±2.7	15.0±1.2	15.0±1.8	14.9±3.5	15.6±3.72	16.4±2.9	18.5±4.0	19.0±2.0	19.6±3.2
O3	24.3±1.0	24.0±0.7	23.8±1.4	22.0±1.1	18.4±1.2	18.3±1.50	17.6±2.1	18.2±0.8	19.7±2.0	22.6±1.7	24.0±0.7	24.0±1.7
BAC	24.2±1.1	23.7±0.7	23.6±2.1	22.1±1.2	18.6±1.2	18.1±1.61	17.2±2.5	18.6±1.4	19.7±2.5	23.1±1.3	24.5±1.0	24.7±0.5
GAC	21.1±2.5	17.4±2.1	17.0±2.7	20.0±2.3	16.4±2.4	16.7±3.07	16.1±3.5	17.1±3.8	17.2±2.1	19.1±4.2	19.1±1.6	20.0±4.7
Fin	19.2±3.2	18.4±3.9	17.0±2.1	19.8±2.8	16.5±2.7	15.5±2.98	15.9±2.9	16.3±4.7	17.4±2.7	18.1±3.3	19.0±1.7	20.3±3.6

Appendix 2

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ETHICAL CLEARANCE CERTIFICATE

Ethical Clearance Reference Number: FOS/135/2016 **Date: 5 December, 2016**

This Ethical Clearance Certificate is issued by the University of Namibia Research Ethics Committee (UREC) in accordance with the University of Namibia's Research Ethics Policy and Guidelines. Ethical approval is given in respect of undertakings contained in the Research Project outlined below. This Certificate is issued on the recommendations of the ethical evaluation done by the Faculty/Centre/Campus Research & Publications Committee sitting with the Postgraduate Studies Committee.

Title of Project: Development of a Model For Identification and Quantification of Algal Toxins in Swakoppoortdam

Nature/Level of Project: Masters

Researcher: H.K. Sakaria

Student Number: 200627104

Faculty: Faculty of Science

Supervisors: Dr.K. Kalili (Main) Dr. E. Julies (co)

Take note of the following:

(a) Any significant changes in the conditions or undertakings outlined in the approved Proposal must be communicated to the UREC. An application to make amendments may be necessary.

(b) Any breaches of ethical undertakings or practices that have an impact on ethical conduct of the research must be reported to the UREC.

(c) The Principal Researcher must report issues of ethical compliance to the UREC (through the Chairperson of the Faculty/Centre/Campus Research & Publications Committee) at the end of the Project or as may be requested by UREC.

(d) The UREC retains the right to:

(i) Withdraw or amend this Ethical Clearance if any unethical practices (as outlined in the Research Ethics Policy) have been detected or suspected.

(ii) Request for an ethical compliance report at any point during the course of the research.

UREC wishes you the best in your research.

Prof. P. Odonkor: UREC Chairperson

Ms. P. Claassen: UREC Secretary