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APPLICATION OF CHLORINE DIOXIDE AS AN ALTERNATIVE PRE-OXIDANT IN THE TREATMENT OF EUTROPHIC RAW WATER

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WILLEM FREDERICK STRYDOM

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Supervisor	**:**	**DR THABO NKAMBULE**
Co-supervisors	**:**	**PROF TITUS MSAGATI**
	:	**PROF BHEKIE MAMBA**

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DECLARATION

Name: Willem Frederick Strydom

Student number: 57670048

Degree: Magister Technologiae Chemical Engineering

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I declare that the above thesis is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

2017/10/18

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DEDICATION

This work is dedicated to my family who have supported me and gave me the strength and inspiration, without which I would not have been able to complete my studies.

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ABSTRACT

The Vaalkop water treatment works (WTW) abstracts water from the Vaalkop Dam, which is situated in the Crocodile West/Marico Water Management Area of South Africa. The bulk of the inflow into the dam is through a canal fed from the Hartebeespoort Dam. The water quality of the Vaalkop Dam was of pristine quality during the time the dam was constructed but has since deteriorated gradually to highly eutrophic. The high nutrient levels have caused high concentrations of NOM, taste and odour problems, leaching of high concentrations of metals and operational problems such as reduced filter run times and high plant water losses. The currently available pre-treatment options have become inadequate to deal with the deteriorating raw water quality and this has prompted an investigation to explore the use of an alternative pre-oxidant in order to address these challenges in the raw water. An assessment of chlorine dioxide (ClO_2) as an alternative pre-oxidant was undertaken. The aim was to investigate the effectiveness and economic viability of using ClO_2 as a pre-oxidant as well as conditions under which ClO_2 should be applied to obtain high quality water.

The ClO_2 was generated on site using the two chemical generation method whereby sodium chlorite is reacted with chlorine gas and the resulting ClO_2 is directly injected into the raw water pipeline. A full scale plant trial was conducted in parallel with lab scale jar test experiments. The trial was conducted over a twelve month period. The operation of the generator was monitored by determining the generation efficiency and dosing adjustments were carried out based on the ClO_2 demand. The water of the various treatment steps and the final water were sampled. Various parameters including NOM indicators, physicochemical and plant operating parameters as well as metal content, disinfection by-product (DBP), bacterial and algal concentrations were monitored.

The two chemical generation method produced an excellent ClO_2 yield of ≥96%, and the produced ClO_2 was generally found to be a very effective pre-oxidant. This technology was used with very little operational interruptions and no safety related incidents were reported during the trial period. When compared with chlorine, the

ClO_2 pre-oxidant proved to be much more effective in the prevention of the formation of DBPs in the final water. Whereas a good algal removal rate of ≥97% was achieved during severe cyanobacterial blooms when ClO_2 was used as a pre-oxidant, the algal removal rate dropped to 93% when the pre-oxidant was changed to chlorine. Compared to Cl_2, a superior taste and odour removal efficiency was achieved when the ClO_2 was used as a pre-oxidant. However, similar removal efficiency towards geosmin and 2-methyl-isoborneol (2-MIB) was recorded for the two pre-oxidants. Therefore, it was concluded that: (i) in addition to geosmin and 2-MIB, other unidentified taste- and odour-causing compounds were present in the raw water; and (ii) the ClO_2 appears to selectively target these unidentified compounds much more effectively than chlorine. In addition, ClO_2 was able to effectively remove the iron and manganese present in the raw water to below the South African National Standard (SANS) 241 limits in the presence of high levels of NOM and the unidentified taste- and odour-causing compounds. Other than leading to the formation of trihalomethanes (THMs), the application of Cl_2 under such conditions has previously proven to be ineffective in the removal of iron and manganese as well as taste- and odour-causing compounds.

Since ClO_2 is much more expensive than Cl_2, the chemical treatment cost increased by 6.8 c/kl at an average dosage of 0.8 ppm when ClO_2 was used as a pre-oxidant. However, this increase seems to be offset by additional benefits such as reduction in coagulant demand and increase in treatment rates during times of severe algal blooms. To this end, an initial economic assessment points to ClO_2 as a viable option for the treatment of raw water of poor quality for potable use.

As evidenced by results obtained from the assessment of water quality and water treatment plant operational parameters, the application of ClO_2 as an alternative pre-oxidant at the Vaalkop WTW was a success. However, Cl_2 still remains the cheaper of the two pre-oxidant (Cl_2 vs ClO_2) and should be applied during periods of reduced organic loading when high rainfall and dam levels are experienced. Chlorine gas is also an efficient and cost effective treatment option to utilise when no taste and odour problems are experienced and low levels of iron and manganese are present in the raw water. Chlorine dioxide is definitely a pre-treatment step of choice during periods of high organic loading when reduced filter run times and high

plant losses are experienced. It should also be applied during drought periods and/or low dam levels. During such periods, high algal concentrations coincide with anaerobic conditions, which is normally associated with high levels of iron and manganese contaminants in the raw water.

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LIST OF ABBREVIATIONS

ACRONYM	DEFINITION
AOM	Algal Organic Matter
AWWA	American Water Works Association
DBPFP	Disinfection By-product Formation Potential
BDOC	Biodegradable Dissolved Organic Carbon
COM	Cellular Organic Matter
ClO_2	Chlorine dioxide
ClO_2^-	Chlorite Ion
DBP	Disinfection By-product
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DPD	N, N-diethyl-p-phenylenediamine
DWS	Department of Water and Sanitation
ELISA	Enzyme-linked Immuno Sorbent Assay
FEEM	Fluorescence Excitation Emission Matrix
FRA	Flavour Rating Assessment
GC	Gas Chromatograph
HAA	Halogenated Axcetic Acids
HDT	Hach Digital Titrator
$KMnO_4$	Potassium Permanganate
2-MIB	2-methyl-isoborneol
ML/d	Megalitres per day
MnO_4^-	Permanganate Ion
$MnO_2(s)$	Manganese Dioxide

MW	Magalies Water
NaClO$_2$	Sodium Chlorite
NEMP	National Eutrophication Monitoring Program
NOM	Natural Organic Matter
NTS	Sodium Thiosulfate
PAC	Powdered activated carbon
PC	Personal Computer
PLC	Programmable Logic Controller
POC	Particulate Organic Carbon
QC	Quality Control
SABS	South African Bureau of Standards
SANS	South African National Standards
SCADA	Supervisory Control and Data Acquisition
SUVA	Specific Ultraviolet Absorbance
TOC	Total Organic Carbon
THM	Trihalomethanes
WHO	World Health Organisation
WMA	Water Management Area
WTW	Water Treatment Works

CHAPTER 1

INTRODUCTION

1.1 Background

The Vaalkop Dam (**25°18'29.02"S; 27°29'01.51"E**) is situated in the Crocodile West / Marico water management area (WMA) of South Africa (**Figure 1.1**). The Hex and Elands rivers provide the natural inflow into the dam, which has a historic average annual yield of 12 million m^3 per annum or 32 ML/d. The natural yield is being augmented by a canal from the Hartebeespoort dam system. The canal was constructed in 1985 and has a maximum capacity of 4 cubic meters per second.[1] The current capacity of the Vaalkop WTW is 270 ML/d and thus requires permanent flow of the canal to prevent the dam level from dropping to critically low levels.
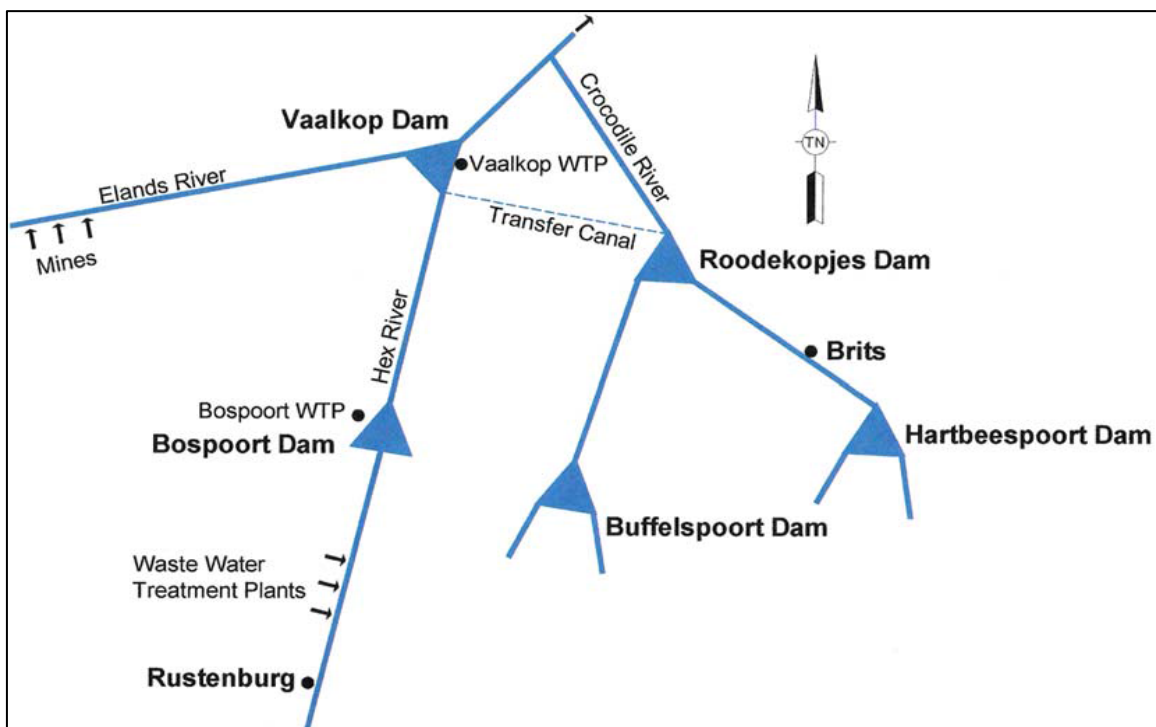
Figure 1.1: The Crocodile West Catchment[2]

1.2   Problem Statement

Raw water sources in South Africa are becoming increasingly under pressure because of increased utilization and pollution in the catchment areas.[3] An estimated 35% of the stored water sources have been classified as eutrophic to hypertrophic.[4] The pollution is causing excessive levels of algae, which complicates the treatment process and causes bad taste and odour in the water. Except for a high nutrient load, sewage pollution from overloaded wastewater treatment works and urban runoff from informal settlements also introduces bacteria, viruses and pathogens like E.Coli, cryptosporidium and giardia.

The water quality of the Vaalkop Dam was of pristine quality during the time the dam was constructed but have since deteriorated gradually to highly eutrophic.[5] The Vaalkop dam is one of 7 dams in the National Eutrophication Monitoring Program of the Department of Water and Sanitation (DWS) that were classified as hypertrophic in 2012.[6] According to the Program, an impoundment is classified as hypertrophic if the mean annual Chlorophyll-a concentration exceeds 30 µg/L and the mean total phosphorus concentration exceeds 0.130 mg/L.[7]

The Bospoort Dam is situated upstream of the Vaalkop Dam on the Hex River. High nutrient loads originating from two sewage treatment works, which discharges into the Hex River, have been reported.[2] These high nutrient loads have caused numerous algal blooms, the presence of cyanobacterial toxins and taste and odour problems at both the Bospoort and Vaalkop WTW.[8]

The main source of pollution of the Elands River is the Seshabele River, which is a tributary to the Elands River and is a high source of salts, ammonia and phosphates. These pollutants originate from the high nutrient levels in the sewage treatment works and the surrounding industrial and mining activities. This is evident from investigations and catchment monitoring activities undertaken by Magalies Water as part of a program to manage the catchment of the Vaalkop Dam.[1]

The Hartebeespoort Dam is situated upstream of the Roodekopjes Dam in the Crocodile River, which feeds the canal that flows into the Vaalkop Dam. The poor

water quality of the Hartebeespoort Dam is well known.[9] The dam is also hypertrophic and experiences annual cyanobacterial blooms and subsequent cyanotoxin release as well as taste and odour problems.[10]

In 2012, a severe cyanobacteria algal bloom was experienced at the Vaalkop Dam during which time more than 10 000 cells/mL was detected in the source water and 6000 cells/mL penetrated into the drinking water.[11] In addition, anaerobic conditions at the abstraction point, taste and odour, manganese and colour problems were experienced during and the existing treatment options was not adequately effective in the treatment of the incoming raw water.

A fish species diversity count conducted in 2009 indicated the absence of papermouth yellow fish. This species respond very quickly to a change in the water quality. It was historically present in the Vaalkop Dam and it's absence provides another indication of the deteriorating water quality of the dam.[12]

The presence of NOM in the source water has the potential to form disinfection by-products (DBPs) when it reacts with oxidants such as chlorine.[13] It has, therefore, become increasingly important to remove the NOM during the treatment process to prevent formation of DBPs due to their possible carcinogenic character.[14] These DBPs include THMs and halogenated acetic acids (HAAs). In South Africa, the allowable amount of THM in the final water is now regulated by the SANS 241: 2015 national drinking water standard, and treatment processes need to be adjusted to ensure compliance of the final water to the standard.[15]

1.3   Justification

The current pre-treatment options available at the Vaalkop WTW are oxidation with chlorine or adsorption with powdered activated carbon (PAC). Oxidation plays a very important role in the potable water treatment train and is usually employed at the head of the treatment plant. The purpose of oxidation is to remove inorganic and organic compounds.[13]

The most significant contaminants present in the raw water source of the Vaalkop WTW are.[5]

- Iron and Manganese

- Colour

- Taste and odour causing compounds

- Chlorophyl-a

- DOC

- E-Coli

- Cryptosporidium and Giardia

In addition, THM has recently emerged as a contaminant in the final water due to oxidation of NOM with chlorine and THM non-compliances to the new SANS 241 standard have been reported.[16] According to the new SANS 241 standard, total THM should now be reported according to its four main constituents. These are listed below in **Table 1.1** together with their concentration limits[15]:

Table 1.1: SANS 241 THM Limits

THM Constituent	SANS 241 Limit (mg/L)
Bromoform	≤ 0.100mg/l
Chloroform	≤ 0.300mg/l
Dibromochloromethane	≤0.100mg/l
Bromodichloromethane	≤ 0.060mg/l

The Vaalkop Dam (see **Figure 1.2**) was constructed in 1971 with a capacity of 55 million m^3 and a surface area of 1110 ha[17].

Figure 1.2: The Vaalkop Dam

As illustrated in **Figure 1.3**, Low dam levels have been experienced over an extended period [18]. The dam is relatively shallow with a wall height of 11.44 m. The level of the dam has ranged between 40 and 60 % during the past three years (2015-2017) and this has necessitated the abstraction of raw water at very low levels. Due to the high volume of raw water augmented from the Hartebeespoort Dam scheme, high nutrient levels have caused high concentrations of NOM in the form of algal blooms. Decomposition of the algae causes anaerobic conditions to develop at the abstraction point, which leaches high concentrations of metals such as manganese into the raw water.
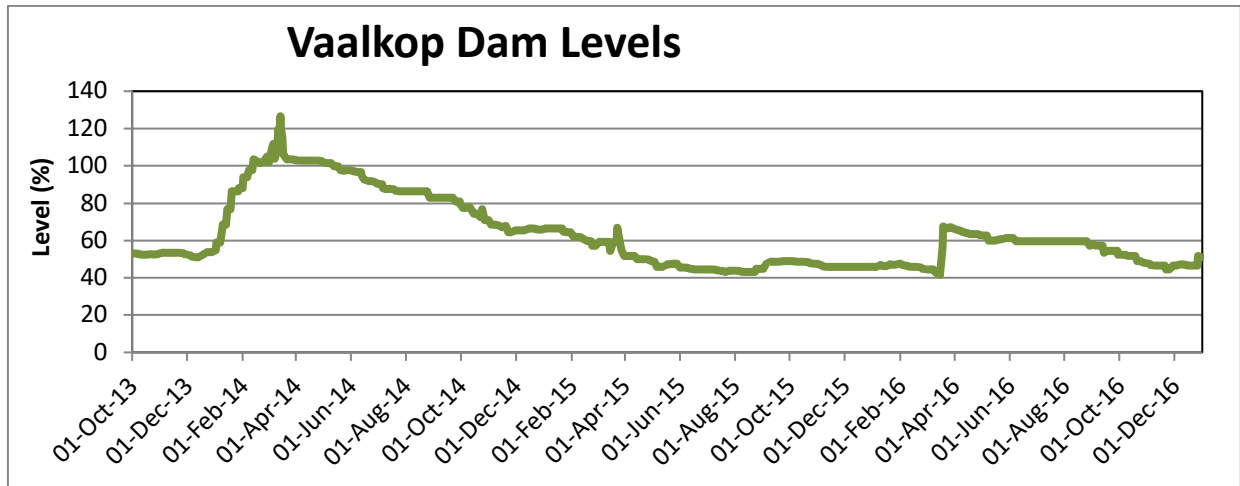
Figure 1.3: The Vaalkop Dam water levels over the past 3 years (2013-2016)

The combination of high manganese and algal concentrations leaves the process controller with the predicament of whether to oxidise the manganese during pre-treatment using chlorine or to make use of the PAC for the adsorption of taste and odour caused by the NOM in the water. The end result is either reduced manganese with taste and odour complaints or reduced taste and odour with colour problems emanating from the manganese and increased chlorine demand at the final disinfection step. Poor removal of either manganese and colour or cyanobacterial species as well as taste and odour causing compounds have been reported during these conditions.[19]

These problems have prompted an investigation to explore the use of an alternative oxidant for the pre-treatment of water in order to address a combination of these challenges in the raw water.

1.4 Aims and Objectives of the study

The aim of the study is:

- To determine the effectiveness of the use of chlorine dioxide as a pre-treatment chemical at the Vaalkop Water Treatment Works when compared to chlorine gas.

- To determine the economic viability (in terms of treatment cost for potable water treatment) of using chlorine dioxide as a pre-oxidant.

- To determine conditions under which the different treatment options should be applied to obtain the most effective and efficient result in terms of final water quality and chemical treatment cost.

1.5 Outline of the Thesis

This dissertation outline summarizes the structure of this dissertation, which is presented as follows:

Chapter 2: Literature Review

This chapter presents a general review of the pre-treatment of raw water for potable consumption. Eutrophication of raw water sources as well as the different options for the pre-treatment of such water is discussed. In addition, the different chlorine dioxide generation options are reviewed as part of a justification for the adoption of the two chemical method for this study. The chapter concludes with a discussion on the significance of NOM in the source water of a drinking water treatment plant.

Chapter 3: Experimental Methodology

In this chapter, all the experimental procedures followed in accomplishing the aims of this project are presented

Chapter 4: Results and Discussions

Results obtained following the experimental procedures listed in the previous chapter are presented in Chapter 4. Specifically, the results of the bench scale experiments and plant trial are scrutinized in more detail.

Chapter 5: Conclusions and Recommendations

This chapter is focussed on the conclusions that could be drawn from the results of this study. These conclusions are then correlated with the intended aims of this study and recommendations on ways of furthering this study are presented towards the end of the chapter.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The main objective of potable water treatment is to produce water that is fit for domestic use, meaning water that is safe for drinking and is aesthetically pleasing. A water treatment plant consists of individual treatment processes that are linked together to produce final water that complies with the relevant regulatory standards. The individual processes are selected and designed according the quality of the feed water.[1]

2.2 Pre-treatment

2.2.1 Background

Chemical oxidation plays an important role in the treatment of water for potable use.[2] There are several steps throughout the treatment process where oxidants may be added, namely pre-oxidation, intermediate oxidation and final disinfection steps.[3] An oxidation step is often added at the start of the treatment process, before or at the rapid mixing basin where coagulation takes place.[2] The addition of an oxidation step before the conventional treatment train is carried out in order to improve the removal of some of the chemical substances present in the raw water. Pre-oxidation usually leads to the elimination of chemically reduced inorganic species such as iron and manganese.[2] Pre-oxidation also assists in the reduction of biological growth in the treatment plant.[4] Numerous studies have shown that the addition of pre-oxidants can improve the removal of algal and cyanobacterial cells by coagulation and flocculation.[5] In addition, an adsorption step may be added in cases where organic pollutants such as geosmin and 2-methylisorboneol (2-MIB) are present. The most common chemicals used during the pre-treatment step (i.e. pre-oxidants) are

chlorine, ozone, potassium permanganate, powdered activated carbon and chlorine dioxide.[6]

2.2.2 Chlorine

Chlorine is the most widely used oxidant and disinfectant for water treatment applications in the world due to the fact that it is relatively inexpensive and widely available.[7] Chlorination has traditionally been used as a pre-oxidant in the water treatment process. However, the discovery of DBP formation during chlorination has led to its demotion as a pre-oxidant of choice.[8] When used as a pre-oxidant, chlorine enhances coagulation.[9] However, in the presence of NOM, the formation of DBPs such as THMs is promoted when chlorine is used as a disinfectant or oxidant.[2]

2.2.3 Ozone

The discovery of the formation of chlorination by-products with adverse health effects has created the need for an alternative effective disinfectant.[10] As a result, ozonation has become a more popular pre-oxidant for application in the removal of taste, odour, colour and micro-organisms prior to the coagulation step because it does not form chlorinated DBPs. Ozone is an unstable molecule and therefore needs to be generated at the point of use for water treatment applications.[6] The generation process involves the circulation of air or oxygen past a high voltage charged electrode.[6] If bromide is present in the water supply, it forms bromate which is a regulated chemical.[8] However, one of the disadvantages of ozone is that the capital cost for initial start-up is very high. The process is also very power intensive and thus increases the treatment cost even more. Ozonation is also a complex technology,[11] which requires a highly skilled maintenance input for consistent operation.[12]

2.2.4 Potassium Permanganate

Potassium permanganate ($KMnO_4$) has been used as an oxidant in water treatment applications for decades.[2] Commercially, it is provided in a crystalline from and is applied to the water by either a dry feeder or a solution is made up on site from the

crystals and then applied with a dosing pump.[2] $KMnO_4$ is primarily used for the removal of colour, iron and manganese in drinking water treatment; it is also to control taste and odour.[6] $KMnO_4$ may also be used as an alternative pre-oxidant for the treatment of eutrophic raw water in order to avoid the formation of DBPs.[13] Pre-oxidation of *Microcystis aeruginosa* with $KMnO_4$ have shown that, unlike other oxidants such as ozone, the $KMnO_4$ did not rupture the cell walls upon oxidation.[5] The organic matter adsorbed on the cell surface is released without causing damage to the cell and leading to lower DBP formation.[5] During the oxidation by KMnO4, the permanganate ion (MnO_4^-) is reduced to insoluble manganese dioxide $(MnO_2(s))$. The $MnO_2(s)$ is a black precipitate, which should be properly removed in the treatment process to prevent the black particulate deposits from entering the distribution system.[2]

2.2.5 Powdered Activated Carbon (PAC)

Activated carbon is a form of carbon that has been oxidized during a carefully controlled process to develop a porous carbon structure with a surface area greater than 500 m^2/g.[14] The raw material used during the production of PAC originates form a wide variety of carbonaceous materials such as wood, coal, lignite and coconut shell.[15] The production process involves the carbonization of the raw material through a pyrolysis process at 500 ^oC in the absence of air.[16] During the pyrolysis process, the raw material is converted to a char and a stream of nitrogen is used as the carries gas.[2] The char is then activated at temperatures between 750 $^{\circ}C$ and 950 $^{\circ}C$ using oxidizing gases such as steam or CO_2.[16] This step eliminates all impurities adsorbed on the surface of the char and an increase in pore size and volume is obtained. The outer surface of the char is simultaneously oxidized leading to formation of the active sites.[16]

PAC is added during the water treatment process to adsorb organic compounds present in the water. PAC dosage may be done periodically in line with seasonal water quality problems (i.e. taste and odour) or continuously, depending on the requirement.[2]

2.3   Chlorine Dioxide

Chlorine dioxide (ClO_2) was discovered in 1811 by Sir Humphrey Davy when he acidified potassium chlorate with sulphuric acid.[17] The first reported application of chlorine dioxide in drinking water treatment was in 1944 at the Niagara Falls Water Treatment Plant in New York, where it was used for the removal of phenolic compounds from the raw water of the Niagara River.[18]

2.3.1   Characteristics of ClO_2

Chlorine dioxide exists as a volatile free radical and it is explosive when exposed to pressures of 40 kPa and above.[19] It is also unstable at high concentrations and is therefore usually produced on site.[6] Unlike chlorine, chlorine dioxide does not hydrolyse when it is mixed with water; instead it remains as a dissolved gas.[2] In addition, compressed chlorine dioxide is shock sensitive and explosive and therefore cannot be shipped in cylinders to site like chlorine.[20]

2.3.2   Methods for the Generation of ClO_2

In water treatment applications, ClO_2 is commonly generated at working concentrations of between 100 mg/L and 3000 mg/L injected into the water to obtain an applied dosage of around 1.5 mg/L.[20] The generation of ClO_2 for application in the treatment of potable water is generally carried out by using sodium chlorite ($NaClO_2$) as the main precursor chemical. The $NaClO_2$ can either be in the solid form (80%) or as a 25% solution.[19] Although the sodium chlorite in solid form needs to be converted to an aqueous form by making up a solution, this is not recommended for onsite use due to handling, storage and safety considerations.[20]

A number of reactions that can be applied for the conversion of $NaClO_2$ to ClO_2 are known.[6] The two chemical method that uses acid and chlorite is described by the following chemical equation:[19]

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \qquad\qquad (2.1)$$
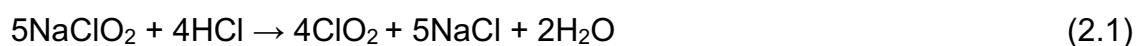
This chemical conversion method has a 20% loss in efficiency due to the five chlorite ions yielding only four chlorine dioxide molecules. Another disadvantage of this system is that some chlorate ions may be formed in the reactor. This is due to the reaction involving the conversion of chlorite to ClO_2, which is not instantaneous and requires several minutes of contact time in the reactor. During this period, some of the formed ClO_2 may react with water to form chlorate, as indicated in the following reaction.[20]

$$6ClO_2 + 3H_2O \rightarrow 5HClO_3 + HCl \qquad\qquad (2.2)$$

The two chemical method that employs chlorine gas and chlorite (see Equation 2.3) is also known.[19]

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \qquad\qquad (2.3)$$

The theoretical efficiency of this reaction is 100% and the reaction is instantaneous, which eliminates the possibility of the formation of chlorate due to extended storage of ClO_2. However, the possibility for the formation of chlorate exists if the pH is reduced to below 3.5.[2] In practice, it is possible to obtain a conversion as high as 98% with a properly calibrated and operated generator. The three chemical method, which involves an acid, bleach and chlorite, is summarized in the following chemical equation:[20]

$$HOCl + 2HClO_2 \rightarrow 2ClO_2 + HCl + H_2O \qquad\qquad (2.4)$$

In this reaction, the acid converts the hypochlorite to hypochlorous acid and the chlorite to chlorous acid. The reaction is not instantaneous and thus requires a large reactor. Compared to the other methods, continuous pH monitoring is essential since a much lower pH should be maintained in order to obtain optimal production of ClO_2. The pH typically needs to be kept around 2.5. Another disadvantage of this method is that chlorates may be formed due to the prolonged storage in the reactor.

2.3.3   Water Treatment Application

Taste and odour control has in the past been one of the primary applications of chlorine dioxide.[2] It has been reported that, although chlorine dioxide is effective for the removal of swampy, grassy and fishy odours, it is ineffective against the removal of odours caused by geosmin and 2-MIB.[6] Chlorine dioxide is effective in the destruction of phenols and other constituents of industrial effluents, which form undesirable taste and odour when treated with chlorine.[21] The oxidation of phenols with ClO_2 results in the formation of chinones and malonic acid. Odorous chlorophenols are, however, not formed.[22] ClO_2 destroys the aromatic and conjugated structures of NOM and transforms large and long chain aromatic and aliphatic organics to small and hydrophilic organics.[23] The oxidation of NOM fractions with ClO_2 also leads to the formation of significant amounts of aldehydes and carboxylic acids.[24]

Pre-treatment with chlorine dioxide improves the turbidity at the outlet of the sedimentation tank when compared to treatment train without chlorine dioxide.[25] Chlorine dioxide is an effective disinfectant and is much more effective than chlorine in the inactivation of most viruses, spores, cysts and ocysts[26]. Another advantage is that its biocidal properties are not affected by the pH.

The advantage of using chlorine dioxide as pre-oxidant is that it improves the coagulation process,[9] but it does not form THMs.[2] Studies carried out by researchers in China on 12 different water sources treated with ClO_2 as pre-oxidant and Cl_2 as final disinfectant revealed that the use of ClO_2 reduced the formation of disinfection by-products by up to 45%.[23] Other studies also indicate that a sharp decrease in the yield of chloroform, chloral hydrate and dichloroacetonitrile was obtained when ClO_2 was used as pre-oxidant in the presence of microcystin LR and subsequent chlorination.[27]

Clogging of filters is a common problem at the Vaalkop WTW during periods of high algal blooms. This is a common problem for many water utilities when filter clogging dominate over other algae and occur mostly during spring when the water is colder.[2] A study was conducted where the inactivation effect of chlorine dioxide and liquid

chlorine on algae and animal planktons were compared.[28] The destructive effect of chlorine dioxide towards algae was found to be far much better than that of chlorine on certain species. Chlorine dioxide was also found to possess a superior inactivation effect towards viruses and animal planktons when compared with chlorine.[28]

Chlorine dioxide has been reported not to be effective in the inactivation of cyanotoxins.[2] A comparative analysis of the reactions involving various oxidants with the cyanotoxins microcystin LR, cylindrospermopsin and anatoxin-a,m revealed chlorine dioxide as not being a suitable oxidant for the inactivation of cyanotoxins due to the low rate constant for reaction of chlorine dioxide with these toxins.[29] Another potential disadvantage associated with the use of ClO_2 is that 50-70% of the product is reduced to the chlorite ion (ClO_2^-). Although chlorite is not regulated in South Africa, it is limited to 1 mg/L in the USA.[25] Yang *et al*. (2013), found that 59% of the applied ClO_2 turned into chlorite and 8% into chlorate.[23] It was also found that the application of 1 mg/L ClO_2 during the pre-oxidation step did not exceed the chlorite limit of 0.7 mg/L when the by-product formation was determined. [23] When used as a disinfectant, chlorine dioxide does not maintain a residual and secondary disinfection is therefore required.[30]

One of the most important properties of chlorine dioxide that makes it suitable for application at the pre-treatment stage is that it is a non-chlorinating oxidising agent. The chlorination of NOM constituents such as humic acids, fulvic acids and other naturally occurring organic substances is thus prevented at the first stage of the treatment process where these compounds are present in very high concentrations. This therefore contributes a reduction in the formation of THMs.[20]

2.4   Eutrophication

Eutrophication is defined as the process of nutrient enrichment of a water body with dissolved chemical nutrients, which stimulates and leads to excessive plant growth and thus resulting in the depletion of dissolved oxygen. The high nutrient concentrations may be caused by natural or cultural activities. Natural eutrophication originates from sources such as soil and rock and occurs naturally

within the catchment area. Cultural eutrophication is a result of nutrients being introduced into the water body by human activities through agricultural (e.g. fertilizers) and domestic activities (e.g. sewage treatment discharge).[31] The two main nutrients derived from human activities that is of concern in eutrophication is phosphorous (P) and nitrogen(N)[32] as these nutrients are essential for the growth of cyanobacteria.[33] Cyanobacterial blooms is a symptom of eutrophication[34] and causes treatment challenges for potable water production in South Africa.[35]. Due to the dependence of cyanobacterial growth rate on temperature, these blooms occur mainly during summer; the optimum temperature for the cyanobacterial growth rate is about 25 ºC.[36]

2.4.1 Phases of Eutrophication

The trophic status of an impoundment is an indication of the extent of eutrophication of the water body. The different stages of eutrophication according to the NEMP are summarised in **Table 2.1**

Table 2.1 Description of Eutrophication State[37]

State	Description
Oligotrophic	Low in nutrients and not productive in terms of aquatic animal and plant life.
Mesotrophic	Intermediate levels of nutrients, fairly productive in terms of aquatic animal and plant life and showing emerging signs of water quality problems.
Eutrophic	Rich in nutrients, very productive in terms of aquatic animal and plant life and showing increasing signs of water quality problems.
Hypertrophic	Very high nutrient concentrations where plant growth is determined by physical factors. Water quality problems are serious and can be continuous.

The trophic status of a water body according to the NEMP is done according to **Table 2.2**. The mean annual chlorophyll a and phosphorus concentrations are used as indicators.

Phosphorus has been found to be the fundamental cause of eutrophication in South Africa of which domestic and industrial effluents are the major sources.[33]

Table 2.2 Trophic Status Indicators[37]

Indicator	Unit	Trophic Status of Impoundment			
		Oligotrophic	Mesotrophic	Eutrophic	Hypertrophic
		(low)	(moderate)	(significant)	(serious)
Mean Annual chlorophyll a concentration (x)	µg/L	$0 < x \leq 10$	$10 < x \leq 20$	$20 < x \leq 30$	>30
		Current nuisance value of algal bloom productivity			
		negligible	moderate	significant	serious
% of time chlorophyll a concentration (x) >30 µg/L	%	0	$0 < x \leq 8$	$8 < x \leq 50$	>50
Mean annual total phosphorus concentration (x)	mg/L	$x \leq 0.015$	$0.015 < x \leq 0.047$	$0.047 < x \leq 0.130$	>0.130
		Potential for algal and plant productivity			
		negligible	moderate	significant	serious

2.4.2   Treatment Related Challenges Associated with Eutrophication

A rise in the cyanobacterial population in the water resource is of concern to the receiving water treatment works, not only due to an increase in cell concentration, but also due to the possible presence of dissolved algal organic matter (AOM) in the raw water.[5] One of the major concerns to water treatment works when cyanobacteria are detected in the raw water source is the metabolites associated with the presence of cyanobacteria.[38] Apart from possible release of taste and odour compounds such as geosmin and 2-methyl-isoborneol (2-MIB),[39] cyanobacteria have the ability to produce toxins such as microcystins, nodularins, cylindrospermopsins and anatoxins,[40] which pose a health risk to both humans and animals.[31] AOM can seriously impair the efficiency of the water treatment process, especially during the decline phase of an algal bloom when high concentrations of cellular organic matter (COM) are released into the source water.[5] One of the most pronounced adverse effects on potable water production and quality during the presence of high concentrations of COM is reduction in coagulation efficiency.[5] In addition, algal blooms could also cause clogging of filters due to their dense cell accumulation,[39] which results in reduced filter run times, increased filter backwashing and higher treatment cost,[35]

2.4.3   Occurrence of Eutrophication in South Africa

Most of the drinking water supplied to communities in South Africa originate from surface water.[41] Algal blooms have been reported in most of the surface water systems in South African due to high levels of eutrophication caused by inadequately treated domestic and industrial effluents, which are being discharged into the catchments.[41] The occurrence of cyanobacterial blooms in South Africa has been reported particularly in the Crocodile (West) and Marico Water Management Areas (WMAs).[33] All impoundments in the Crocodile West Catchment are considered to be hypertrophic (i.e. eutrophic),[41] and the catchment of the Vaalkop Dam is located in the same WMA. The Vaalkop Dam is one of the seven dams in the National Eutrophication Monitoring Program (NEMP) of the Department of Water and Sanitation, which were classified as hypertrophic in 2012.[42] According to NEMP,

an impoundment is classified as hypertrophic if the mean annual Chlorophyll-a concentration exceeds 30 µg/L and the mean total phosphorus concentration exceeds 0.130 mg/L.[31]

2.5 Natural Organic Matter

Natural Organic Matter is a heterogeneous mixture of undefined and structurally complex organic compounds,[43] which are derived from the degradation of plants, animals and microbial residues and their waste and metabolic products.[44] The NOM concentration in the source water can be estimated by measuring the dissolved organic carbon concentration of the source water, which typically ranges between 2 and 15 mg/L.[44] Particulate organic carbon (POC) is defined as NOM in the particulate form and is determined by subtracting the dissolved organic carbon from the total organic carbon (TOC).[2] The largest contributor to POC in lakes and reservoirs is algae.[2] The presence of NOM is raw water sources causes serious problems during water treatment and the general conclusion is that NOM should be removed during the treatment process.[45]

2.5.1 NOM Related Challenges and Removal during Water Treatment

Both the quantity and composition of NOM affect their removal during potable water treatment, and it is very important to characterize NOM to optimize the treatment process for its removal.[45] Conventional techniques for the removal of NOM include coagulation, sedimentation and sand filtration and in some instances advanced treatment processes such as enhanced coagulation and ozonation.[46] Most NOM is, however, difficult to remove because its composition is not well understood and the character of NOM is not easily determined.[44]

Pollution of water by organic compounds, of which NOM is the major contributor, creates major problems during water treatment. The effect of NOM on water quality and the potable water treatment processes is illustrated in **Table 2.3**.[2]

Table 2.3 Effects of NOM on Quality and Treatment

Characteristic	Significance
Aquatic humic matter.	Imparts natural colour
Coats inorganic particles in water supplies.	Affecting particle stability
Contributes to alkalinity for waters high in humic matter.	Alkalinity is mostly die to inorganic carbon
Source of taste and odour	Impacts aesthetic quality
DBP precursors	Formation of DBPs
Metal Complexation	Increases metal solubility
Reacts with metal coagulants	Increase in coagulant demand
Reacts with metals	Affect precipitation of metals
Reacts with oxidants	Creates an oxidant demand
Fouling of activated carbon	Increase dosage / treatment cost
Reacts with disinfectants	Creates disinfectant demand
Decreases effectiveness of UV disinfection	Increased disinfection cost, bacterial non-compliances
Provides carbon source	Biofilm growth in distribution system

One of the major problems is proliferation of micro-organisms and subsequent deterioration of microbiological quality in the distribution system.[43] NOM can also impart colour.

When the removal of biodegradable dissolved organic carbon (BDOC) was tracked in the treatment train in a water treatment plant in Namibia, 47% of the BDOC was removed during the sand filtration process.[43] Pre-ozonation was utilized during this case study in Namibia. In another case study in Poland, the use of chlorine dioxide as an oxidant was compared with ozone in terms of BDOC formation after reaction with NOM.[22] The reaction of chlorine dioxide with NOM was found to form BDOC such as aldehydes and short chain carboxylic acids. The BDOC is then consumed by bacteria and can cause regrowth in distribution systems if the oxidation of the NOM takes place after sand filtration.[22]

2.5.2 Techniques for the Measurement and Characterisation of NOM

The term natural organic matter is normally used to designate all the organic matter present in a reservoir or ecosystem, excluding synthetic compounds such as organic micropollutants.[47] Due to the fact that the NOM found in natural waters is composed of an extremely complex group of compounds measurements and characterisation and are often not undertaken on pure compounds, but rather characterised by a group of compounds fractionated from the waters using various techniques.[47] The NOM in natural waters consist of hydrophobic and hydrophilic fractions. Hydrophobic acids are generally the largest fraction of NOM and can comprise approximately 50% of the TOC.[48] The hydrophobic acids are humic substances consisting mainly of humic and fulvic acids. Hydrophobic fractions of NOM comprise aromatic carbon, phenolic structures and conjugated double bonds.[48] The hydrophilic fractions of NOM consist of aliphatic and nitrogenous compounds such as carbohydrates, sugars and amino acids.[48]

2.5.2.1 Dissolved Organic Carbon (DOC)

In Practice, NOM is usually represented by the measurement of TOC, DOC or UV_{254}. An operational definition of DOC is the organic carbon content of a water sample after being filtered through a 0.45 µm filter.[49]

2.5.2.2 UV$_{254}$ Measurements

UV$_{254}$ has been shown as a good predictor of DOC and TOC concentrations in water.[2] It also serves as a surrogate parameter for DBP precursors, particularly with relation to THM formation potential.[50] A close correlation has also been found between UV$_{254}$ and the hydrophobic content of DOC.[50] The absorbance at 254 nm is associated with the aromatic groups and therefore there is a tendency for the absorbance of UV$_{254}$ to only represent the aromatic character of NOM.[49]

2.5.2.3 Specific Ultraviolet Absorbance (SUVA)

The specific ultraviolet absorbance (SUVA) of a sample is defined as the ultraviolet absorbance of the sample divided by the DOC concentration of the sample.[49] SUVA gives an indication of the composition of NOM present in the water.[2] A high SUVA value (>4) indicates the presence of high molecular weight NOM, which give rise to high oxidant demand and subsequent high percentage removal (60-80%) of the TOC by coagulation. Such a value also indicates that the NOM is of hydrophobic[8] and aromatic nature.[49] Conversely, a low SUVA value (<2) is indicative of the presence of low molecular weight NOM, which give rise to low oxidant demand and subsequent low percentage removal (<20-40%) of TOC by coagulation.[2] The NOM composition is comprised mainly of the hydrophilic fraction.[49]

2.5.2.4 Fluorescence Excitation Emission Matrix (FEEM)

Several methods exist for the characterisation of NOM, but they are often time consuming and involve sample preparation.[45] Fluorescence spectroscopy is a technique that has gained popularity in the for characterisation of NOM for water treatment purposes.[51] The advantage of the technique is that it is a rapid and sensitive method, which requires a small volume of sample without any sample preparation before analysis.[52] The fluorescence excitation emission matrix (FEEM) method is used to classify different NOM components and to distinguish them from each other.[53] **Figure 2.1** shows the FEEM peaks of NOM, which have been grouped into five different regions for qualitative purposes.[54]
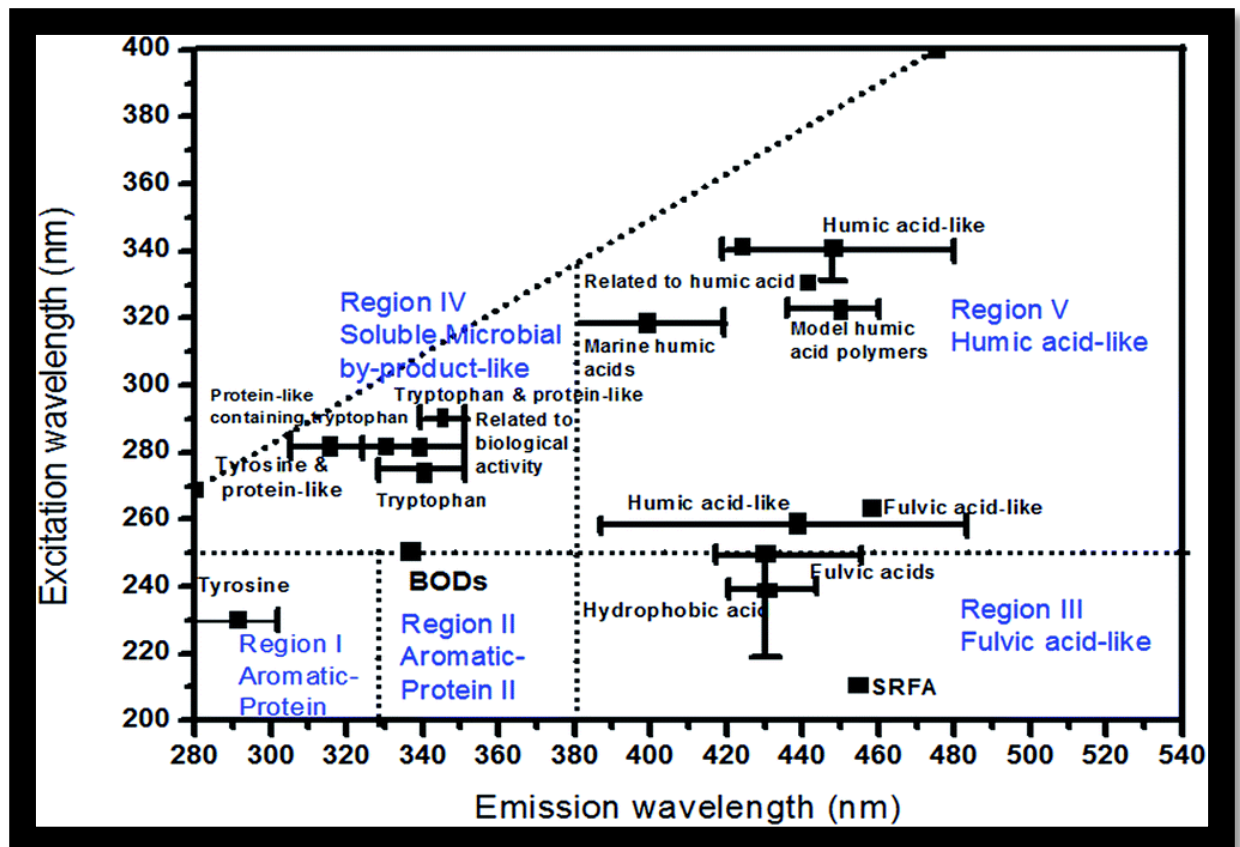
Figure 2.1 FEEM Peak Regions[54]

2.6 Source Water Parameters of Concern

The two key challenges faced by the Vaalkop WTW personnel in the selection of an appropriate pre-treatment technology are as follows:[6]

- There are instances when taste and odour problems coincide with high concentrations of iron and manganese. In such cases, a choice between PAC and chlorine needs to be made. When pre-chlorination is adopted as part of the water treatment process, the taste and odour compounds are not removed. When PAC is adopted as part of the treatment train to deal with the taste and odour problems, there is no pre-oxidation and this leads to poor removal of iron and manganese.

- The Vaalkop distribution system traverse an area of more than 500 km and difficulties are often experienced in the maintenance of adequate chlorine

residual, especially when the PAC is dosed in the pre-treatment step. The requisite chlorine demand is thus not met during the pre-treatment step.

2.6.1　Source Water Impoundment Characteristics

2.6.1.1 Stratification

The Vaalkop Dam is a relatively shallow impoundment with an overflow height of 11.41 m as was discussed in **Chapter 1 (section 1.3)**. Fluctuating dam levels and thermal stratification are some of the physical factors that could have an effect on the water quality of the Dam. The chemistry of lakes and rivers are significantly influenced by the occurrence of thermal stratification, which is one of the key processes influencing the water quality.[55] Stratification of an impoundment determines the conveyance of oxygen and nutrients between the surface and the bottom layer and influences the light environment of phytoplankton cells[56]. During the summer period, dams and lakes stratify into three zones, which are summarised in **Table 2.4**.[2]

Table 2.4 Stratification Zones

Stratification Zone	Description
Epilimnion	Top Layer, in contact with the atmosphere allowing mixing by wind, light penetration and exchange of gasses.
Metalimnion	Transition zone which separates the warmer Epilimnion form the cold water in the bottom zone.
Hypolimnion	Bottom zone which is separated from the atmosphere contains the cold dense water, little mixing takes place.

Dam turnover occurs in autumn when the epilimnion cools down and the change in density causes the top water to sink and mix with the metalimnion. The metalimnion eventually erodes with further decline in temperature and circulation as mixing takes place.[2]

2.6.1.2 Iron and Manganese

The phenomenon of global warming has become a reality and is predicted to continue into the future.[55] Consequently, aquatic eco systems are increasingly subjected to warmer temperatures and fluctuating rainfall patterns.[57] Droughts may cause a deterioration in water quality of impoundments when intense drawdown is experienced which may cause an increase in salinity, increase in nitrogen and phosphorous concentrations.[55] This can lead algal blooms and a decrease in the dissolved oxygen (DO) concentration of the hypolimnion. The hypolimnion rapidly turns anoxic or anaerobic and large amounts of pollutants such as iron and manganese accumulate in the bottom zone.[55] The epilimnion on the other hand is high in DO concentration and at elevated pH levels due to the high algal concentrations. The soluble iron and manganese is oxidised into insoluble forms and precipitates downwards into the hypolimnion.[58] Under anoxic conditions in the hypolimnion, the iron and manganese undergo a reduction and transforms into a soluble state.[2] Due to low dam levels, there is a risk of deterioration in quality of the entire water column during dam turnover.[57]

2.6.2   Disinfection By-products (DBPs)

DBPs have become a focus of attention since being identified as having adverse health effects when present in the drinking water supplies.[8] From more than 600 DBPs that have been identified, THM and HAA are the most common. Fractionation studies have indicated that the high molecular weight fraction and hydrophobic components of NOM contributes the most towards the THM formation potential.[50] The hydrophobic fraction on its own can however not be used as an indication of the disinfection by-product formation potential (DBPFP) due to the transphilic fraction of NOM, which can also contribute significantly to the DBPFP.[50]

2.6.3   Taste and Odour

One of the major problems associated with the presence of high concentrations of algae in the source water of a water treatment works is production of taste and odour compounds.[2] A selection of algae and their associated odours are listed in **Table 2.5**. The most common taste and odour chemical produced by algae are geosmin and 2-MIB. These metabolites are mainly produced during cyanobacterial blooms.[36] An analysis on the historical data from algal identification analysis from the Vaalkop Dam indicates that cyanobacteria are the dominant species during summer seasons leading into autumn when generally higher temperatures are experienced.[36] During winter, the dominant species were found to be Dinophyceae for the years 2005-2008. The dominant species during the winter months changed for the years 2009-2010 when Chlorophyceae and Bacillariophycaeae comprised the majority of species identified in the Vaalkop Dam raw water.[36]

Table 2.5 Taste and Odours Caused by Presence of Algae.[2]

Class	Associated Taste and Odours
Cyanobacteria (Blue-Green Algae)	
Anabaena	Earthy, musty
Microcystis aeruginosa	Earthy, musty
Oscillatoria	Earthy, musty
Chlorophyceae (Green Algae)	
Chorella vulgaris	Musty
Scenedesmus quadricauda	Grassy
Staurastrum	Grassy
Bacillariophycaeae (Diatoms)	
Asterionella	Geranium
Fragillaria	Geranium
Tabellaria	Geranium
Dinophyceae (Pigmented Flagellates)	
Ceratium	Fishy
Dinobryon	Violet
Peridinium	Cucumber

2.7   Conclusion

Application of ClO_2 as pre-oxidant could be appropriate to eliminate taste and odours generated from sources other than geosmin and 2-MIB.[6] It also has the potential to oxidise iron and manganese and reduce the formation of DBPs. The ClO_2 project at Vaalkop WTW was conducted as a pre-treatment step to eliminate the possibility of BDOC formation after the filtration process and subsequent bacterial growth in the distribution system. The application of ClO_2 as pre-oxidant in the removal of DOC was then compared with that using chlorine and ozone.

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CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1   Introduction

This chapter gives a detailed account of the experimental procedures that were carried out in order to attain the objectives of this study.

3.2   Area of Study

Magalies Water owns and operates the Vaalkop, Klipdrift, Cullinan and Wallmannsthal Water Treatment Plants. The Magalies Water area of supply is illustrated in **Figure 3.1**. This study was conducted at the Vaalkop WTW, which is situated approximately 50 km northwest of Brits in the North West province of South Africa. The Vaalkop water treatment works supplies mainly bulk potable water services in the municipal areas of Rustenburg, Moses Kotane and Thabazimbi. The Vaalkop WTW has a treatment capacity of 270 ML/d and is divided into three separate treatment units, which are summarised in **Table 3.1**.

Table 3.1: Description of the Vaalkop WTP

Plant	Capacity/	Unit processes Employed	Process Diagram
Plant 1	30 ML/d	Pre-Ozonation; chemical dosing; flocculation; dissolved air floatation (DAF); intermediate ozonation; sand filtration; granular activated carbon filtration; chlorination.	Figure 3.2
Plant 2	90 ML/d	Pre-chlorination (current); chemical dosing; flocculation; DAF; sedimentation; sand filtration; chlorination; chloramination.	Figure 3.3
Plant 3	150 ML/d	Pre-oxidation ClO_2 (trial); chemical dosing; flocculation; sedimentation; Intermediate chlorination; counter current dissolved air floatation filtration (COCODAFF); chlorination; chloramination	Figure 3.4

In this study, chlorine dioxide dosing was implemented as a pre-oxidant on the Plant 3 portion of the plant (**Figure 3.4**) and compared with the Plant 1 portion (**Figure 3.2**) which uses ozone as pre-oxidant and Plant 2 (**Figure 3.3**) which uses chlorine gas.
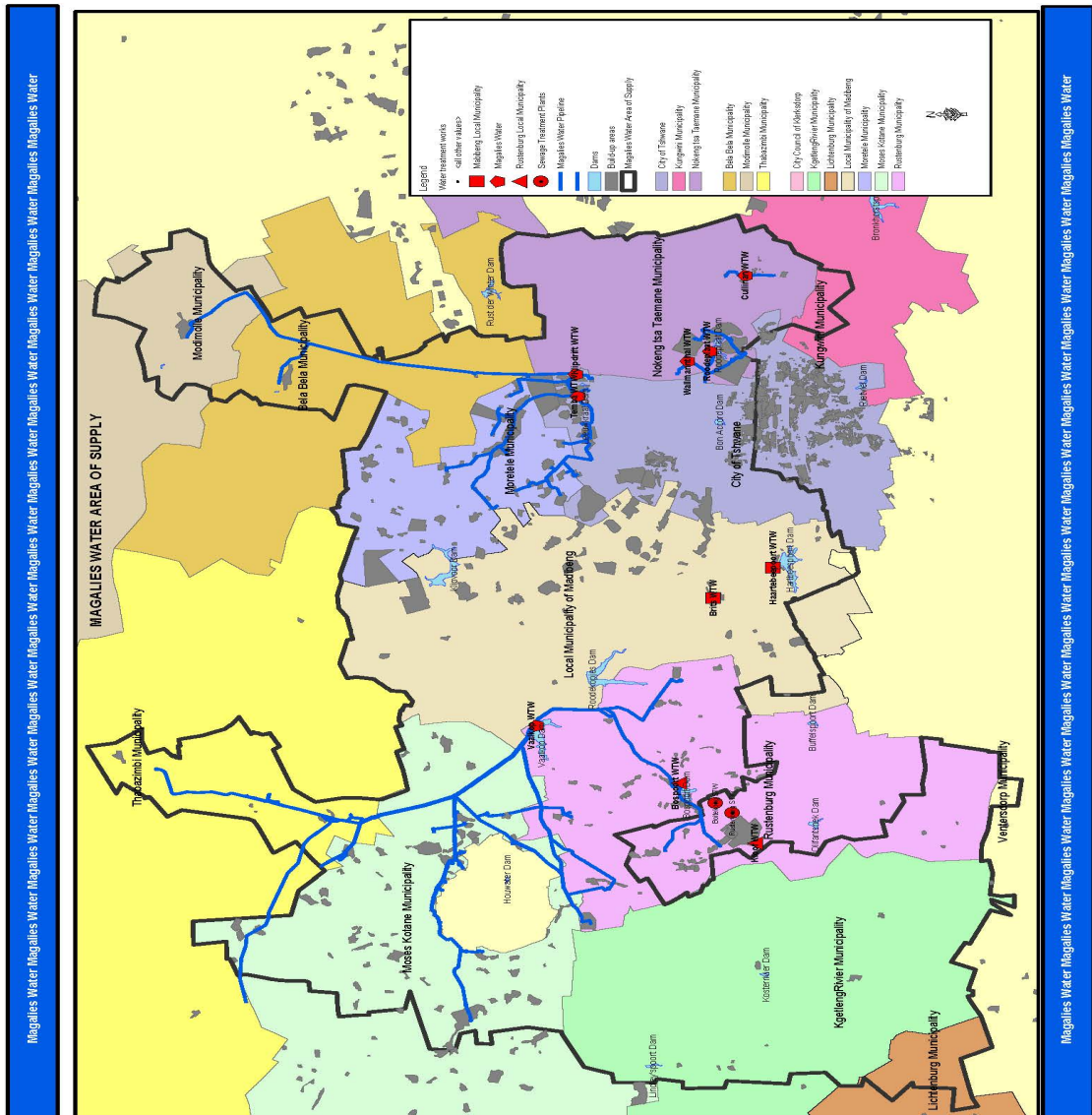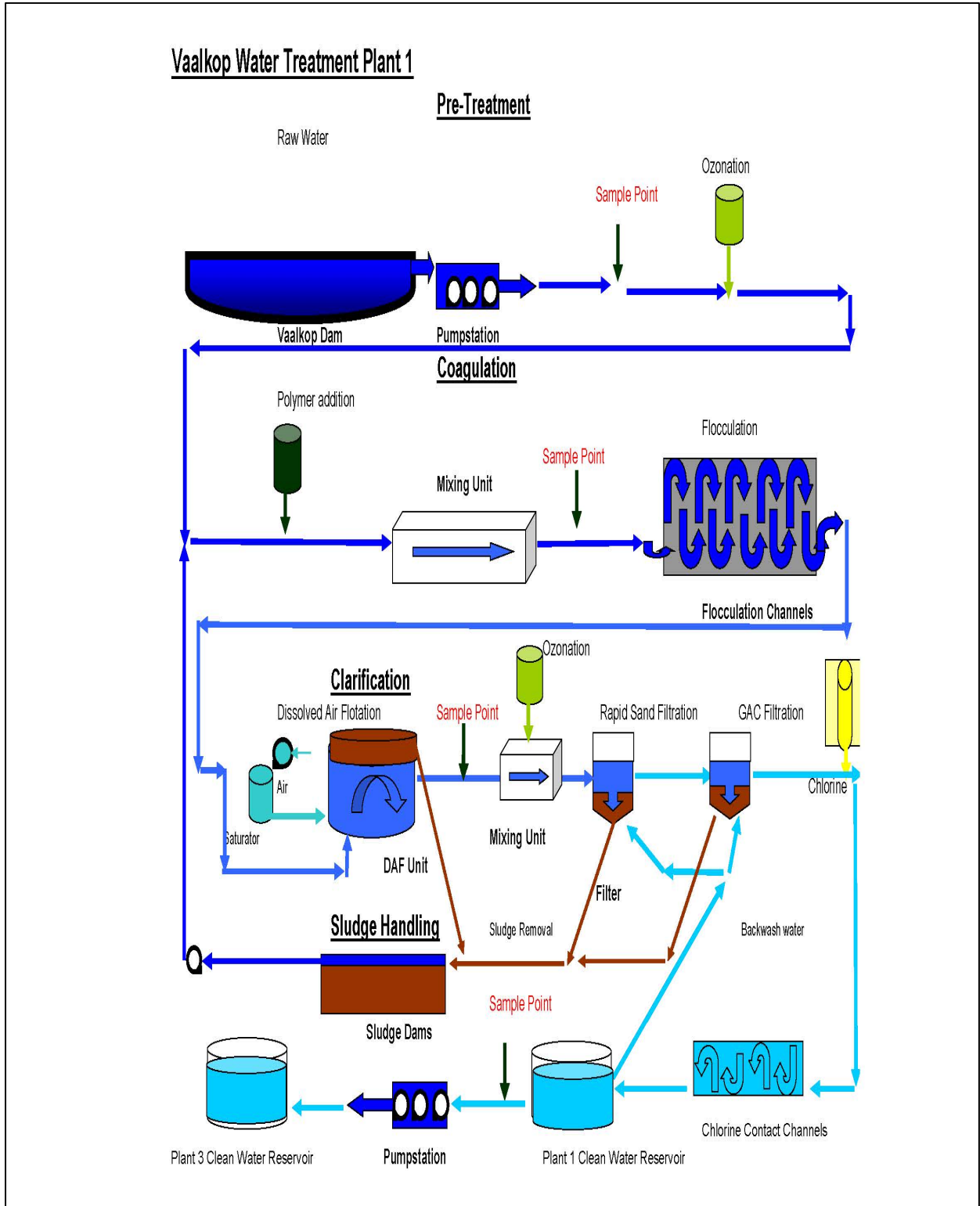

Figure 3.1: Magalies Water Area of Supply

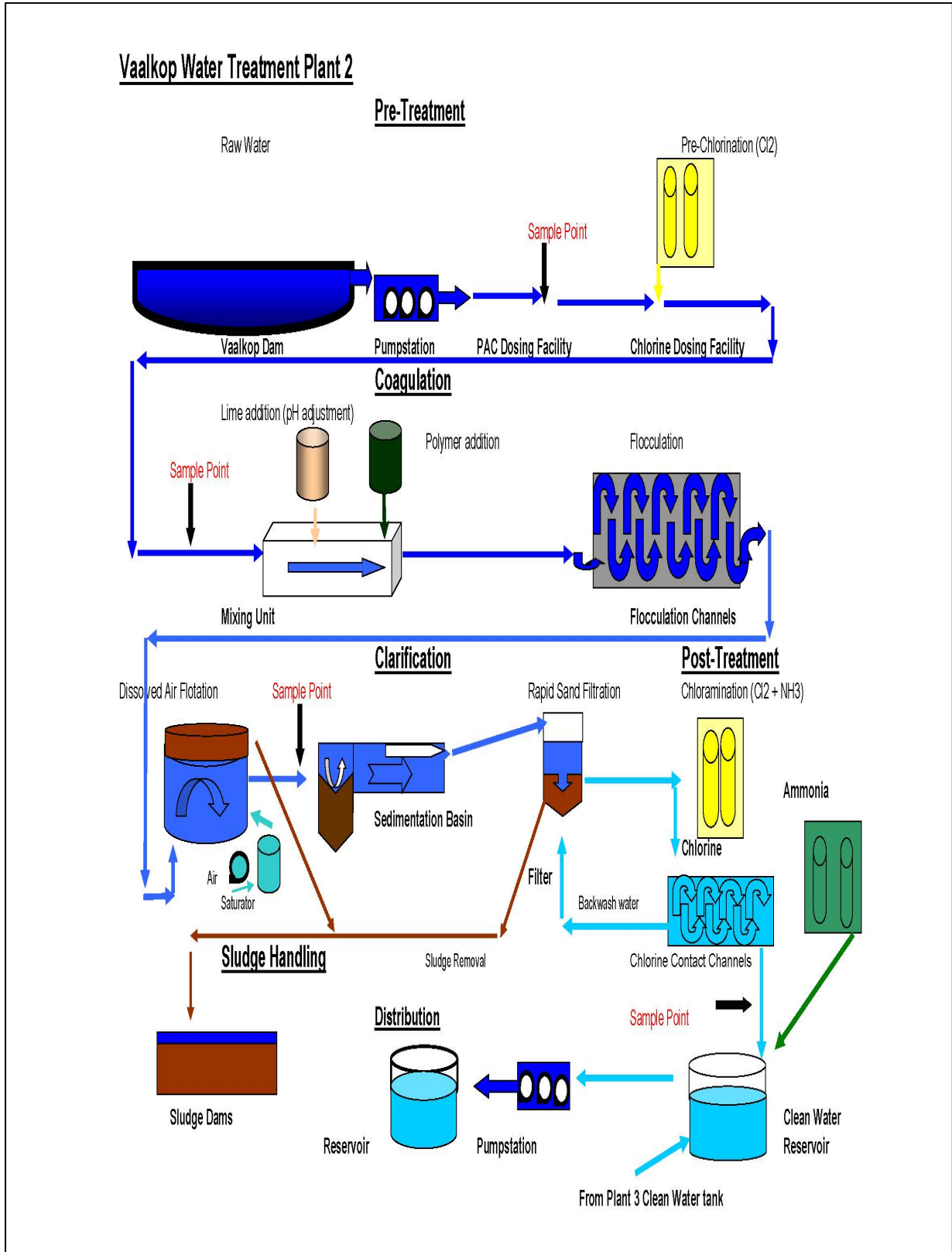**Figure 3.2: Process Diagram of Vaalkop WTW Plant 1**

Figure 3.3: Process Diagram of Vaalkop WTW Plant 2
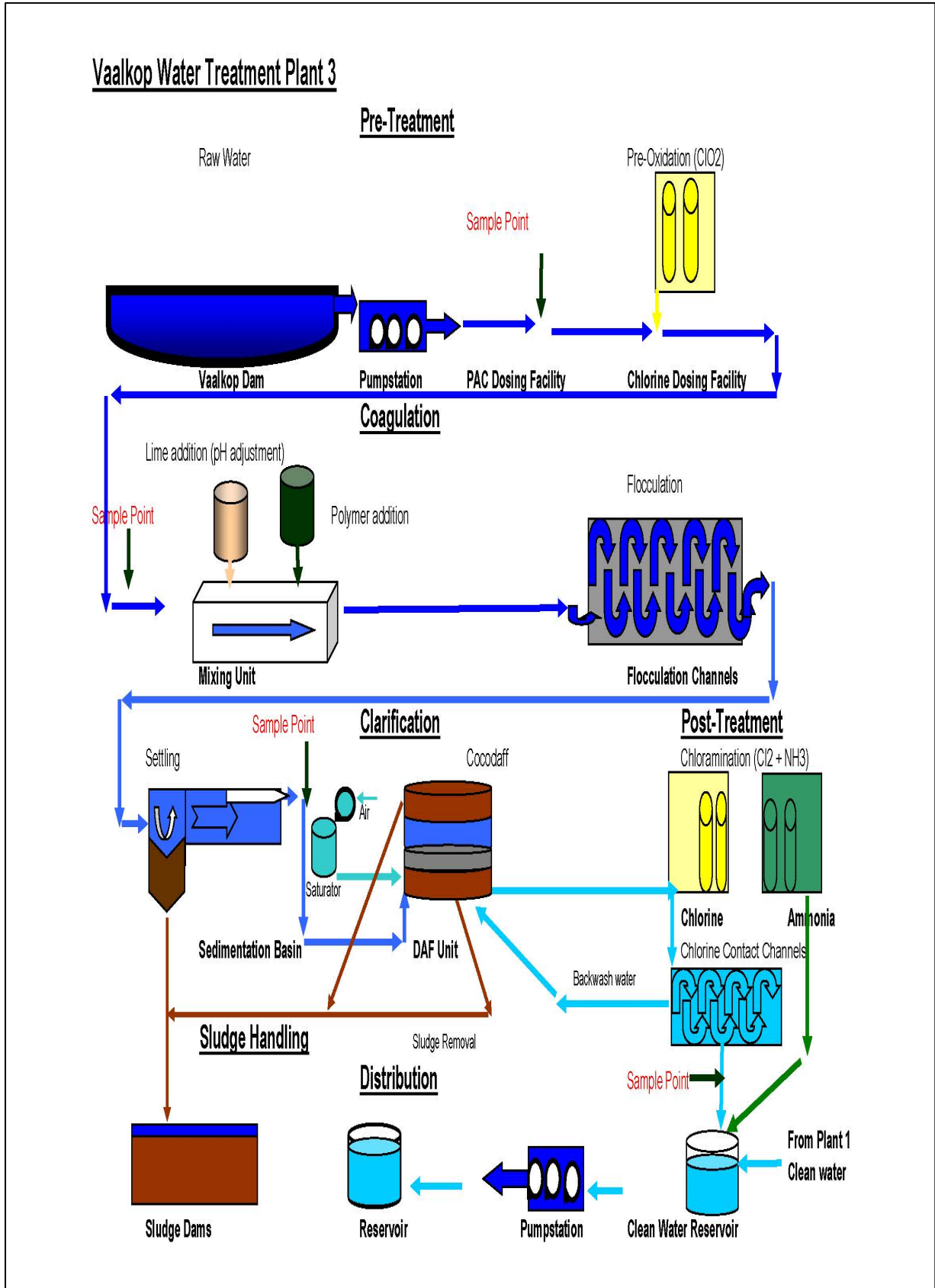
Figure 3.4: Process Diagram of Vaalkop WTW Plant 3

3.3   Chlorine Dioxide Generation

Blendtech in partnership with DuPont Water Technologies was appointed to supply the chlorine dioxide generation equipment. The selected generator (i.e. the DuPont Oxychlor generator) utilises the two chemical method of chlorine gas and sodium chlorite to generate chlorine dioxide. The chemical reaction is as follows:[1]

$$2NaClO_2 + Cl_2\,(g) \rightarrow 2ClO_2\,(g) + 2NaCl \tag{3.1}$$

An initial trial period of 6 months was agreed upon during which a minimum of 49 tons of chlorine dioxide was to be utilized based on an average treatment rate of 180Ml/d and average chlorine dioxide dosage of 1.5mg/l.[2] The initial trial period was then extended by a further 6 month period to enable the gathering of more experimental data over a one year period including all seasons.

The generator was operated according to a comprehensive operating manual supplied by DuPont, which contains general operating instructions, troubleshooting and maintenance requirements.[3]

During the trial period, the chlorine dioxide residuals were monitored and theoretical dosages from the equipment programmable logic controller (PLC) were verified by manual titration.

Apart from the plant trial, bench scale studies, which involved sampling concentrated chlorine dioxide from the generator and utilizing it in jar test experiments, were conducted simultaneously.

3.4   Plant Trials

As mentioned in **section 3.3**, chlorine dioxide was generated on site, and dosing points were installed at the raw water pump station on three separate process streams that feed Plants 2 and 3. For comparison purposes, the ClO_2 feed to Plant 2 was closed and Cl_2 gas was used as a pre-oxidant at Plant 2 while ozone and ClO_2 were used at Plants 1 and 3, respectively.

3.5   Parameters Analysed and Test Methods Used

3.5.1   Chlorine Dioxide Concentration (Generated Product)

The concentrated chlorine dioxide was sampled from the generator in an amber glass bottle using DuPont Water Technologies method AM-100-17 rev A.[4] The concentrated sample, which has an approximate concentration of 1000 ppm, was then diluted 10 times as prescribed in **Table 3.2** from DuPont Water Technologies method AM-100-07 rev E.[5]

Table 3.2: Chlorine Dioxide Stock Solution Guide

Anticipated ClO_2 or ClO_2^- (ppm)	Sample Dilution	Sample Size (ml)	Approx. amount of DI water (ml)
≤ 2	None	200	0
5	None	100	100
100	None	5	195
200	None	2	198
500	1:10	10	190
1000	1:10	5	195
1500	1:10	5	195
≥ 2000	1:10	2	198

3.5.1.1 Titration Method

The chlorine dioxide concentration produced by the generator was determined by conducting a series of titrations with a Hach digital titrator (HDT) on the ClO_2 solution according to DuPont Water Technologies analytical method AM-100-07 rev E.[5] The titration was also used to determine the concentrations of precursor chemicals present in the sample.

Reagents:

The following reagent were used: Sodium Thiosulfate (NTS), 0.113 N (Hach); Dissolved Oxygen Powder Pillow (Hach); Phosphate pH 7 Buffer Solution (Hach); Potassium Iodide Powder (Hach); and Starch Solution (Hach)

Unsparged Sample:

An appropriate amount of deionised water (see **Table 3.2**) was placed into a 250 mL flask. A volume of 2 mL of pH 7 buffer solution was added and swirled. The required amount of the sample was added (see **Table 3.2**) by pipetting the sample beneath the surface of the solution. Two potassium iodide powder pillows were then added and the HDT was zeroed. Using the HDT, the sample was titrated to a faint yellow colour using NTS. 1ml of starch solution was added to the sample and turned turn blue.

Titration of the sample with NTS was continued to the end point when solution became clear.

Reading A was recorded: (digits / 800) / sample size. The HDT was zeroed and 1 dissolved oxygen powder pillow added to the above sample. The sample was placed sample in the dark for 5 minutes. The sample was then titrated with NTS to the end point when the solution became clear. Reading B was recorded: (digits / 800) / sample size.

Sparged Sample:

The sample was sparged with the following procedure:

The gas sparging system was set up according to **Figure 3.5**. An adequate amount of sample was placed into the degassing vessel. A volume of 2 mL of pH 7 Phosphate was added to the sample. The gas dispersion tube was placed into the degassing vessel. The Nitrogen tank was slowly opened until a slow, steady stream of gas bubbles was formed. The sample was degassed for a minimum of 5 minutes.
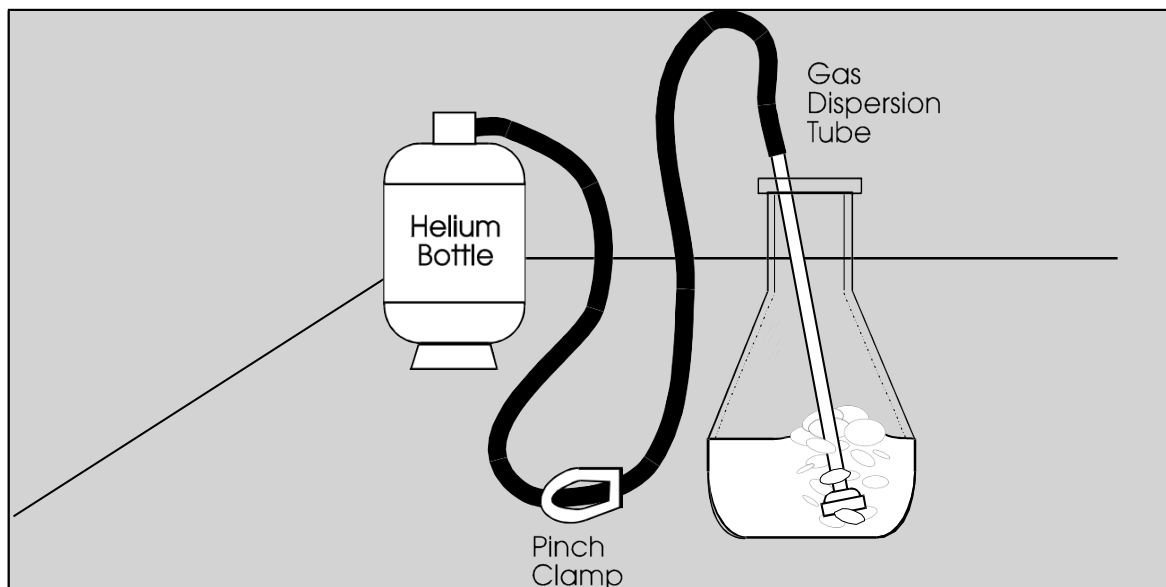
Figure 3.5 Sample Sparge Equipment

The required amount of sample w a s a d d e d (see **Table 3.2**) by pipetting the sample beneath the surface of the solution. One potassium iodide powder pillow was added and the HDT was zeroed. Using the HDT, the sample was titrated to a faint yellow colour with NTS. A volume of 1ml of starch solution was added to the sample and it turned blue. Titration of the sample with NTS was continued to the end point (i.e. when solution became clear).

Reading C was recorded: (digits / 800) / sample size. The HDT was zeroed and 1 dissolved oxygen powder pillow was added to the above sample. The sample was placed in the dark for 5 minutes. The sample was then titrated with NTS to the end point (i.e. until the solution became clear). Reading D was recorded: (digits / 800) / sample size.

Calculations

The respective amounts of chlorite, chlorine dioxide and chlorine were calculated as follows:

Chlorite, mg/L: D x N x 16,863.

Chlorine Dioxide, mg/L: (5/4) x (B - D) x N x 13,490

Chlorine, mg/L: (A – [(B – D) / 4]) x N x 35,453

3.5.2   Bench Scale Tests

3.5.2.1 Chlorine Dioxide Demand

The ClO_2 demand was tested according to the American Water Works Association (AWWA) method 2350C.[6] The ClO_2 stock solution prepared according to section 3.5.1 was dosed at a concentration of 5 mg/L into a raw water sample. A contact time of 10 minutes was allowed and the residual ClO_2 concentration was measured using method as described in **section 3.5.2.2**. The difference between the initial concentration and the residual concentration was recoded as the raw water ClO_2 demand.

3.5.2.2 Chlorine Dioxide Residual

The Hach DR890 colorimeter that has a 10ml glass sample cell was used for the determination of the chlorine dioxide residual.[7] The stored program for the determination of ClO_2 residual with the N, N-diethyl-p-phenylenediamine (DPD) method was entered by pressing the PGRM button followed by 112 and Enter button on the colorimeter keypad. The instrument was first calibrated by filling the 10ml sample cell with the sample to be measured, placing the sample cell in the instrument sample cell compartment, covering the sample cell with the instrument cap and pressing the zero button. Four drops of Hach glycine reagent were then added to the sample cell and swirled to mix. The contents of one DPD free chlorine powder pillow was then added to the sample cell, capped and swirled to mix. Any undissolved powder was allowed to settle for 30 seconds. After placing the sample cell in the instrument sample cell compartment and covering the sample cell with the instrument cap, the read button was pressed. Thereafter, the instrument displayed the concentration of ClO_2 in mg/L.

3.5.2.3 Jar Tests

Phipps and Bird 6 place jar stirrer with 2L plastic jars was used for conducting the jar test experiments. Principles of jar test experiments listed in the American Water Works Association guidelines were used.[8] Concentrations of the ClO_2 were varied

and samples were be taken before and after filtration and analysed for physical parameters as well as DOC and UV_{254} measurements. The concentration of ClO_2 used in the jar tests was informed by the results from the ClO_2 demand tests on the raw water. Using 1.5 mg/L of ClO_2 as a baseline concentration, the concentration of ClO_2 was increased or decreased at 0.5 mg/L intervals, starting with a blank (beaker number 1) and increasing the concentration all the way to 2.5 mg/L (see **Table 3.3**).

Table 3.3: Jar Test ClO_2 Concentrations

Beaker No.	ClO_2 Concentration/ mg/L
1. (Blank)	0
2.	0.5
3.	1.0
4. (Baseline)	1.5
5.	2.0
6.	2.5

The treatment process was simulated whereby the ClO_2 was first added as pre-oxidant and thereafter stirred for 7 minutes at 140 rpm. This was then followed by an addition of the coagulant to the mixture, which was stirred for a further 2 minutes at the same speed. After conditioning for 8 minutes at 40 rpm, the mixture was allowed to settle for 10 minutes and settled water was sampled before filtering using an MN615 filter paper. The following parameters were measured on the settled and filtered water: Turbidity, pH, DOC, UV_{254}, SUVA and $chlorophyll_{665}$.

The aim of the bench scale studies was to test the ClO_2 at different concentrations. This is much easier than doing it at plant scale where changes in pre-oxidant concentrations could affect the final water quality in a negative way.

3.5.3   Chlorophyll 665

To determine the chlorophyll 665 from the jar test samples, a known volume of the sample (0.5 L to 2.5 L) was filtered (in duplicate) through a glass fibre filter (Whatman GF/C) using a glass measuring cylinder.[9] The volume of the sampled used was dependent on the density of the phytoplankton. Prior to filtration, the samples were agitated to ensure uniformity. The glass measuring cylinder and the filtering cup were also rinsed with deionised water before use. The filter and the entrapped phytoplankton were removed without disturbing the phytoplankton or tearing the filter. The filter was then gently rolled without applying pressure.

After placing the filter in a marked screw-capped test tube (20 mL), approximately 10 mL of methanol was added using the methanol bottle top dispenser or appropriate pipette. The test tubes were placed for ±1 hour at 60ºC in a water bath. After 1 hour the test tubes were shaken vigorously (using the vortex shaker at setting ±7 for ±15 seconds) before decanting the extract into marked centrifuge tubes. At this point, the extract was centrifuged for ±5 minutes at ±4800 rpm (to clarify the extract). The absorbance readings were recorded at 660 nm and 750 nm wavelengths using the Hach DR6000 UV/VIS spectrophotometer.

The following formula was used for calculating the chlorophyll-665 (total pigment) from the experimental data:

$$E = \frac{10^6 \text{ x A}(A_{665} - A_{750}) \text{ x Ve}}{Vm \text{ x L}} \tag{3.2}$$

where E = Chlorophyll-665; A = Absorption coefficient of 0.0133; A_{665} = Absorbance at 660 nm; A_{750} = Absorbance at 750 nm; Ve = Volume of solvent (mL); Vm = Volume of sample (mL); and R = Path length of cuvette (cm)

3.5.4   Dissolved Organic Carbon

A Shimadzu Total Organic Carbon TOC-L analyser, which has adopted the 680 $^{\circ}$C combustion catalytic oxidation method, was used for the determination of the DOC. The method involves the oxidation of organic carbon in the sample with heat and a catalyst to form carbon dioxide, and it uses an infrared detector. Samples were filtered through 0.45 µm filters and the instrument was calibrated with a 1000mg/l potassium hydrogen phthalate solution.

3.5.4.1 Experimental Procedures

A 1000 mg/l potassium hydrogen phthalate (KHP) solution was used as a calibration standard.

Preparation of Organic Carbon Stock Standard:
Potassium hydrogen phthalate (HOCOC$_6$H$_4$COOK) was dried at 45°C for 1 hour. In a 1000 ml volumetric flask, 2.125 g of potassium hydrogen phthalate was dissolved in ~800 ml of deionized water and made up to the mark.

Preparation of Inorganic Carbon Stock Standard

The following procedure is for the preparation of 1000 mg/L Sodium Hydrogen Carbonate/ Sodium Carbonate (NaHCO$_3$/Na$_2$CO$_3$) Standard: In a 500 ml volumetric flask, dissolve 1.75 g NaHCO$_3$ and 2.205 g Na$_2$CO$_3$ was dissolved in ~300 ml deionised water and made up to the mark. This method requires the instrument to be calibrated with primary standards every 6 months.

Analysis Procedure:

40ml of the calibration standard was transferred into the vial for calibration, blanks, quality controls and all samples to be analysed.
The instrument was turned On, then OK was clicked on the User dialog box that popped up.

A new sample table was created by clicking on New icon on the tool bar.

The method was set up by browsing and selecting the method of interest then pressing Open.

After selecting the method then press Next.

The required number of samples was entered, the starting point was identified and the Finish button was pressed.

The sample names were updated and the PC and instrument was connected by pressing on Connect followed by Start to begin with analysis. After the samples were analysed the results were displayed in the dialog box.

Calculation and Reporting of results:

The instrument utilizes a microprocessor that will calculate the concentration of carbon based on the absorption of light in the CO_2. The amount of total organic carbon will be expressed in mg/L.

3.5.5   Turbidity Measurements

Turbidity is a measure of the suspended matter in a liquid caused by solids, particles and other pollutants. Turbidity measurement provides an indication of the clarity of water and water quality. The Hach 2100AN turbidity instrument with 25ml sample cell was used for measuring turbidity. Light from a tungsten lamp is passed through the sample. Particles present in the sample causes the light to scatter and this scattered light is detected by a 90° and back scatter detector while light which passes through the sample is detected by transmitted and forward scatter detectors.

The following procedure was used for calibration and verification purposes of the instrument:[10,11]

Primary calibration procedure:
The instrument was calibrated using Stablcal vials before analysis using the following procedure:

The clear filter module for turbidity was inserted into the instrument.
The CAL/Zero button was pressed which initiated the calibration mode.

The turbidity value of the dilution water used in previous calibration was displayed. The Stablcal vial labelled <0.1 NTU was wiped with lens tissue and placed into the cell holder. The cell cover was closed and the Enter key was pressed.

The instrument display counted down from 60 to 0, and recorded the measurement. The instrument automatically incremented to the next standard of 20.00 NTU. The <0.1 NTU vial was removed from the cell holder.

The Stablcal vial labelled 20.00 NTU was wiped with lens tissue and placed into the cell holder. The cell cover was closed and the Enter key was pressed.

The instrument display counted down from 60 to 0, and recorded the measurement. The instrument automatically incremented to the next standard of 200.0 NTU. The 20 NTU vial was removed from the cell holder.

The Stablcal vial labelled 200.0 NTU was wiped with lens tissue and placed into the cell holder. The cell cover was closed and the Enter key was pressed.

The instrument display counted down from 60 to 0, and recorded the measurement. The instrument automatically incremented to the next standard of 1000 NTU. The 200 NTU vial was removed from the cell holder.

The Stablcal vial labelled 1000 NTU was wiped with lens tissue and placed into the cell holder. The cell cover was closed and the Enter key was pressed.

The instrument display counted down from 60 to 0, and recorded the measurement. The instrument automatically incremented to the next standard of 4000 NTU. The 1000 NTU vial was removed from the cell holder.

The Stablcal vial labelled 4000 NTU was wiped with lens tissue and placed into the cell holder. The cell cover was closed and the Enter key was pressed.

The instrument display counted down from 60 to 0, and recorded the measurement. The instrument automatically incremented to the next standard of 7500 NTU. The 4000 NTU vial was removed from the cell holder.

The Stablcal vial labelled 7500 NTU was wiped with lens tissue and placed into the cell holder. The cell cover was closed and the Enter key was pressed.

The instrument display counted down from 60 to 0, and recorded the measurement.

The CAL/Zero button was pressed. The instrument made a calculation based on the new calibration data, stored the new calibration and returned to measurement mode.. The primary calibration was only performed if the instrument did not meet the verification specifications as described below.

Calibration verification:

Instrument verification was performed using Hach verification standards and the procedure is described below:

The < 0.1 NTU Standard was removed from the plastic case and set aside.
The remaining standards was left in the case and was inverted for 2-3 minutes.
The standards were left to stand undisturbed for 5 minutes.
The < 0.1 NTU Standard vial was inserted in the cell holder and the value was read.

If the value was within $\pm$ 10% of the stated vial value, the instrument was validated for reporting purposes. If the reading was not within $\pm$ 10%, the instrument was recalibrated.

Turbidity measurement procedure

The correct filter module assembly was inserted in the instrument. The filter assembly for turbidity has a clear lens while the filter assembly for colour measurement has a yellow metallic coloured lens.

The sample cell was filled to the line (approximately 30ml) with the sample.

The sample cell was handled by the top, and it was capped.

The sample cell was held by the cap, and wiped with lab tissue to remove water spots and finger prints.

The sample cell was placed in the instrument cell compartment, and the lid was closed.

The reading was given time to stabilise and the lowest reading was recorded after the reading stabilised.

3.5.6   pH Measurements

The Hach HQ40D pH instrument with refillable pH electrode, pH 7 and 10 buffers and 250 mL glass beaker for sample measurement was used for pH measurements.

The instrument was calibrated using the pH 7 and pH 10 buffers on a daily basis before commencing with the analysis. The calibration and sample measurement was performed according to the following procedure:[12,14]

3.5.6.1 Calibration

The following procedure was used for the calibration of the pH electrode:[1,2]

The calibration key was pressed.

The display showed the buffer values to be measured.

The probe was rinsed in deionised water and placed in the pH 7 buffer solution.

The read key was pressed. When the reading was stable, the display highlight the buffer that has been read.

The probe was rinsed in deionised water and placed in the pH 10 buffer solution.

The read key was pressed.

The slope value was displayed. The green/ right key was pressed to store the calibration. The slope value should be less than -54%, if the slope was larger than -54%, the calibration was repeated.

3.5.6.2 Sample Measurement

The following procedure was used for the pH measurement:

The pH probe was placed into the sample.

The read key was pressed.

The display showed "stabilizing" and the progress bar filled from 0 to 100% as the probe stabilised in the sample.

When the reading was stable, the lock icon appeared and the result was stored automatically.

The results were recorded and the procedure was repeated for additional measurements.

3.5.7 Electrical Conductivity

Electrical Conductivity is a measure of the ability of water to conduct an electric current. It provides an indication of the amount of dissolved ions in a solution and is

measured in milli siemens per meter (mS/m). The electrical conductivity was measured using the Hach HQ40D instrument with conductivity electrode.

The instrument was calibrated each time before use. The calibration and measurement procedures are described below:[12,15 ,16]

3.5.7.1 Calibration

The probe was rinsed with deionised water and placed in the 1413 µS/m standard solution.

The calibration button was pressed followed by the read key.

When the reading was stable, the Up key was pressed.

The green/ right key was pressed to store the calibration.

The Up key was pressed to go back to the display.

3.5.7.2 Measurement

The conductivity probe was placed into the sample.

The read key was pressed.

The display showed "stabilising" and the progress bar filled from 0 to 100% as the probe stabilised in the sample.

When the reading was stable, the lock icon appeared and the result was stored automatically.

The results were recorded and the procedure was repeated for additional measurements.

3.5.8 UV_{254}

Hach DR6000 UV/VIS Spectrophotometer – The samples were passed through a 0.45 um filter and placed in a quartz cell with 1 centimetre path length. The UV absorbance was then measured at 254 nm and reported in cm^{-1}.[6]

3.5.9 Specific Ultraviolet Absorbance (SUVA)

SUVA was calculated according **to Equation 3.3** by dividing the UV absorbance by the DOC and multiplying by 100 to obtain a result for SUVA in units of L/mg-M.

$$\text{SUVA} = \frac{(\text{UV}_{254} \text{ in cm}^{-1}) \text{x } 100 \frac{\text{m}^{-1}}{\text{cm}^{-1}}}{(\text{DOC in mg/l})} \qquad (3.3)$$

Where:

UV$_{254}$ is the sample absorbance at 254 nm

DOC is the sample DOC concentration in mg/l

3.5.10 FEEM

Fluorescence excitation emission matrix measurements were conducted using a Horiba AquaLog Spectrometer. The spectrometer displays a maximum emission intensity of 1000 arbitrary units (AU). The spectrometer uses a xenon excitation source and excitation and emission slits are set to a 10 nm band pass. To obtain FEEMs, excitation wavelengths were incrementally increased from 200 nm to 600 nm at 5 nm band pass; for each excitation wavelengths, the emission at longer wavelengths is often detected at 0.3 nm steps. To partially account for Raleigh scattering, the fluorometer's response to a blank solution were subtracted from the fluorescence spectra of the sample to be analysed. De-ionised water, with known concentrations of DOC, was used as a blank solution. Absorbance of light from the lamp by DOC molecules in the sample were accounted for by using an inner-filter correction applied to the data by using UV-Vis spectral data from the blank. The AquaLog is equipped with a reference detector to monitor and ratiometrically correct both the excitation source's spectrum for the emission detector and the absorbance signals. A transmission detector is attached to the AquaLog's sample compartment to record the sample's transmission/absorbance spectrum under the same spectral-band pass and resolution conditions as the fluorescence EEM data. The corrected EEM's were then plotted using Origins Lab, supplied with the instrument, with 20

contour lines, each contour interval representing 1/20th of the maximum fluorescence intensity.[23]

3.5.11 Iron and Manganese

A Thermo Fischer X Series II ICP-MS was used to determine the concentrations of iron and manganese present in the samples. An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding quartz "torch" that supports and confines the plasma. The sample aerosol is generated in a nebulizer and sprays chamber and is carried into the plasma through an injector tube located in the torch. The sample aerosol is injected directly into the ICP. Ionization of a high percentage of atoms produces ionic emission spectra.

Preparation of Iron and manganese standards:

As shown in **Table 3.4**, each of the seven calibration standards was prepared in a 1000 mL volumetric flask. A multi element 1000 µg/L standard solution which also contain iron and manganese was prepared by pipetting 1ml of a 1000 mg/L trace metals multi element primary standard into a 1000 mL volumetric flask containing about 500 mL deionised water and was made up to the mark with deionised water. The working standards were prepared by using 1000 mL volumetric flasks, pipetting the amounts to produce the different concentrations as contained in **Table 3.4**.

Table 3.4 Iron and Manganese Calibration Standards

Analyte	Units	Calib Std 1	Calib Std 2	Calib Std 3	Calib Std 4	Calib Std 5	Calib Std 6	Calib Std 7
Amount pipetted	µL	5	30	60	75	150	250	500
Iron	µg/l	5.00	30.00	60.00	75.00	150.00	250.00	500.00
Manganese	µg/l	5.00	30.00	60.00	75.00	150.00	250.00	500.00
End Volume	mL	1000	1000	1000	1000	1000	1000	1000

Quality Control (QC) Standards:

Three QC standards were prepared for quality control purposes. A 1000 ppb intermediate solution was prepared by pipetting 10 mL of a 100mg/l trace metals stock solution into 1000 mL volumetric flask containing about 500 mL deionised water and made up to the mark with deionised water. Respective volumes (15 mL, 80 mL and 200 mL) of the 1000 ppb intermediate solution were then pipetted into three separate 1000 mL volumetric flasks containing about 500 mL deionised water and this was followed by addition of 5 mL concentrated nitric acid and the solution was made up to the mark with deionised water.

Analysis:

The instrument was switched ON, by pressing the button on the side of the instrument. The argon gas was opened and pressure was checked (500-600 kPa). The extraction fan was switched ON. The tubing was checked to sure that it is properly inserted. The chiller was switched On. The computer was switched ON. The Plasma-Lab icon was clicked on the PC. The system started up automatically and the status of the instrument appeared on the screen.

The experiment was set up by clicking on experiment, choosing existing experiment and selecting the iron and manganese experiment. The experimental data was saved with a new name and the results from the previous experiment were deleted. The sample identity was entered on the Sample Information Editor. The Plasma was turned on and the instrument was left to warm up for 30 minutes. The experiment run was started. After all samples were analysed, the calibration was viewed by clicking on results followed by calibration curve and refresh. The results were viewed by clicking on results followed by numerical values and then pressing the refresh icon.

3.5.12 Plant Operating Parameters

Potential positive spinoffs from the pre-oxidation with ClO_2 were monitored as follows:

Filter run times – The filter levels operating philosophy in the plant are constant head operation, which automatically controls the water level at a certain percentage (92%) by varying the outlet valve open percentage by means of electric actuators connected to a PLC.[17] Filters are being backwashed after filtration has been performed for a certain period of time, defined as the filter run time. The run time is determined by monitoring the percentage at which the outlet valve has to open to maintain the filter level at 92%. A clean filter would have a high potential filtration rate and would require the outlet valve to be open at a smaller percentage to maintain the level at 92% than a clogged filter which require the valve to be open bigger to maintain the same filtration rate. The maximum percentage at which the valve opens is 65% after which a backwash is necessary to prevent the filter from overflowing. The filter run time is set on the supervisory control and data acquisition (SCADA) system and a backwash sequence will initiate once the time has run out. Run times were monitored by checking the percentage opening of the outlet valve to maintain the filter level. If the percentage opening of the valve reaches 65% before the filter is due to backwash, the run time is too long and the filter will start overflowing before the backwash starts. This is an indication that the run time setting on SCADA needs to be reduced to prevent water losses and overloading of the other filters in the process train.

Treatment cost for the pre-oxidation with ClO_2 and chlorine – this was determined for the duration of the trial and compared in cents per kilolitre.

Plant production rate – this was determined by reading the plant outflow meters on a monthly basis and was compared with the treatment rates using chlorine gas as pre-oxidant.

The level of the Vaalkop dam – this was monitored by reading the gauge plate at the dam wall and converting into a percentage from the Department of Water and Sanitation (DWS) conversion table.[18]

3.5.13 Sampling Program

Samples were taken for analysis for the parameters listed below at plant 1, plant 2 and plant 3 process streams for comparison purposes. Sampling was undertaken according to the Department of Water Affairs and Forestry guidelines for sampling from a river, stream, lake, dam, reservoir, borehole or point of use.[19]

The following points were sampled:
- Vaalkop canal
- Raw water before pre-treatment (Plant 1,2 and 3)
- Raw water after pre-treatment
- DAF Outlet (plant 1 and 2)
- Sedimentation tank outlet (plant3)
- Final water before Mixing (plant 1, 2 and 3)
- Distribution network

The canal sample is significant due to the fact that it supplies the largest part of inflow into the Vaalkop dam. The raw water sample and canal sample will be compared to establish similarities, if any, between the two sampling points.

The raw water after treatment and subsequent treatment train samples were used to determine the degree of removal of the pollutants under investigation by the different treatment steps.

3.5.14 Trihalomethane (THM) Constituents - Bromoform, Chloroform, Dibromochloromethane and Bromodichloromethane

The liquid-liquid extraction gas chromatographic (GC) method (AWWA standard method 6232B) was used.[6]   Standards of the different THM constituents are

prepared from known standard concentration solutions and injected into the instrument. Calibration curves were drawn and the samples were run. The GC MS library was used to identify the different peaks from the samples and the curves used to quantify the concentrations.[20]

3.5.14.1 Apparatus and Reagents

The following apparatus and reagents were utilized for the analysis of THMs: Gas chromatography/Mass spectrometry (Agilent 7890A Plus GC and an Agilent 5975 MS) coupled with purge and trap; Helium – Ultra High Purity (99.999%); Methanol (CH_3OH); 100 µg/mL Trihalomethane calibration mix; 200 µg/mL Trihalomethane quality control; and
Ascorbic acid purchased from Sigma Aldrich.

3.5.14.2 Experimental Procedure

Preparation of the stock standard solution:
From the commercially available (100 µg/L) mixed THM standard, stock standard solutions were prepared and thoroughly mixed in a 10 mL calibrated and stoppered volumetric flask. The contents were transferred into an appropriate glass container and labelled (i.e date prepared and concentration (10 µg/L)). The standard solution was stored in a refrigerator at 5°C $\pm$ 2°C. From the stock standard prepared above, working calibration standards were prepared as indicated in **Table 3.5**.

Preparation of Quality control (QC) standard solutions:
QC standard solutions with concentrations of 0.05 mg/L were prepared in the same way as the stock standard solution but using a stock solution obtained from a different supplier.

Calibration procedure:

Calibration curves were generated by analysing spiked Milli-Q water. Calibration curves were only accepted when the correlation coefficients are greater than or equal to 0.950; a quadratic regression analysis may also be used. The calibration standards were prepared by spiking 10 mL milli-Q water with the required amounts of the stock solution as indicated in **Table 3.5**.

Table 3.5 Preparation of THM Calibration Standards.

Standard concentration (mg/L)	Volume of working stock spiked in µL:
Blank	0
STD 0.005	5
STD 0.01	10
STD 0.05	50
STD 0.1	100
STD 0.2	200

Instrument setup and analysis:

The analysis sequence was set up on the GC-MS PC (Agilent 7890A Plus GC and an Agilent 5975 MS). The MS was auto tuned as required by selecting View then clicking Tune and Vacuum control, then selecting Tune, then Autotune, then selecting Tune evaluation.

Thereafter, 10ml of sample was transferred into vials and sealed using a new septum each time to ensure proper sealing and to minimise cross-contamination. This was done for the blanks, calibration standards, quality controls and samples to be analysed.

The vials were then loaded into the auto sampler and a calibration curve was prepared by selecting the calibration option on the PC program, entering the standards and corresponding concentrations and starting the calibration.

The samples were than analysed by setting up the program, entering sample names and numbers and starting the analysis sequence.

After analysis, the THM compounds were identified by matching both the retention times and the presence and ratio of the qualifying ion. Quantification of compounds was done by means of the calibration curve generated.

3.5.15 Microcystin Toxin Analysis

The enzyme-linked immuno sorbent assay (ELISA) method was used for the determination of the microcystin concentration in the raw and potable water.[21]

3.5.15.1 Apparatus and Reagents

The following apparatus and reagents were required for the analysis of the microcystin toxin: Adjustable micropipette 20 μL – 200 μL with disposable tips; Envirologix microtiter plate reader; Envirologix microtiter plate washer; Envirologix orbital plate shaker with incubator; Timer; Vortex shaker; and Parafilm; Envirologix Microcystin Toxin ELISA kit containing: (i) Antibody-coated microwell plate; (ii) 12 removable strips of 8 micro wells each, in resealable foil bag with desiccant; (iii) Negative control; (iv) Calibrators (0.1 ppb, 0.3 ppb, 0.6 ppb and 1.2 ppb); (v) Assay diluent; (vi) One packet of wash solution salts; (vii) Microcystin – enzyme conjugate; (viii) Substrate; and (x) Stop solution.

3.5.15.2 Experimental Procedure

The wash solution was prepared by adding the contents of the wash solution salts to a 1000 mL volumetric flask and making up to the mark with distilled water.

All reagents and antibody coated microwell strips were allowed to reach ambient temperature (18°C to 24°C) before commencing with the test. The strips should not be removed from the bag with desiccant until it has reached ambient temperature).

The microtiter plate reader was calibrated prior to commencement of the analysis. The automated washer and incubator were set up. All samples, reagents and pipettes were arranged so that pipetting could be performed in 10 minutes or less (as per instruction received with each kit). The amount of removable strips required was determined and were placed on a separate frame. The unused strips and the desiccant was resealed in the plastic bag provided.

The strips were marked with the sample names. One strip can accommodate four samples in duplicate. Thus, when analysing four samples in duplicate, two strips were required as the negative control and three calibrators occupied the first removable strip and the actual samples the second removable strip.

All the reagents were mixed well on a vortex shaker for approximately 10s prior to use. The pipette was set at 125 µL and 125 µL of microcystin assay diluent was rapidly pipetted to each well (direction: top to bottom, from left to right). All unused test kit components were replaced into cooler box immediately after use.

The pipette volume was reset to 20 µL, the timer started and add 20 µL of negative control, 20 µL of each calibrator and 20 µL of each sample were added into their respective wells (each with their own pipette tip). This was done in duplicate (two wells below one another assigned to one sample). The wells were covered with parafilm to prevent evaporation and thereafter incubated at ambient temperature while thoroughly mixing the contents of the wells at 200 rpm for approximately 30 minutes. The timer was reset after incubation of approximately 30 minutes. The pipette was reset to 100 µL, the timer started and then 100 µL of microcystinenzyme conjugate added to each well. The wells were covered with parafilm to prevent evaporation and incubated at ambient temperature while thoroughly mixing the contents of the wells at 200 rpm for approximately 30 minutes.

After incubation, the timer was reset, the plate covering was removed and then the plates were washed with the automated microtiter plate washer with wash

solution. The timer was started and 100 µL of substrate were added to each well. The wells were covered with parafilm to prevent evaporation and incubated at ambient temperature while thoroughly mixing the contents of the wells at 200 rpm for approximately 30 minutes. The stop solution (100 µL) was added to each well and mixed thoroughly for approximately 30 seconds on the bench-top. The contents of the wells turned yellow. The plates were read with the micro plate reader within 30 minutes of the addition of stop solution. The plate reader expresses the microcystin concentration in µg/L.

3.5.16 Taste and Odour Measurements

Taste:

The flavour rating assessment (FRA) test was conducted according to standards method 2160C.[6] The scale of rating according to **Table 3.6** was used to assess the taste of final water sample:

Table 3.6 Flavour Rating Assessment Criteria

Rating Scale	Description
1	I would be very happy to accept this water as my everyday drinking water.
2	I would be happy to accept this water as my everyday drinking water.
3	I am sure that I could accept this water as my everyday drinking water.
4	I could accept this water as my everyday drinking water.
5	Maybe I could accept this water as my everyday drinking water.

6	I don't think I could accept this water as my everyday drinking water.
7	I could not accept this water as my everyday drinking water.
8	I could never accept this water as my everyday drinking water.
9	I can't stand this water in my mouth and I could never drink it.

Odour:

Samples were placed in 500ml capped glass bottles and heated in a water bath. The samples were then agitated by shaking, the cap was removed and the vapours were sniffed. The samples were rated according to **Table 3.6**.

3.5.17 Geosmin and 2-MIB

The geosmin and 2-MIB concentrations of the raw and final water was determined by purge and trap coupled to gas chromatography - mass spectrometry (Agilent 7890A Plus GC and an Agilent 5975 MS).[9]. Standards of different known concentrations of Geosmin and 2-MIB were prepared and injected into the instrument. Calibration curves were drawn and the samples are run. The GC MS library was used to identify the different peaks from the samples and the curves was used to quantify the concentrations.

Preparation of Stock Standard Solutions:

From the commercially available (100 µg/mL) mixed Geosmin and 2-MIB standard, a stock standard solution was prepared by making up 1 mL into 10 mL of methanol in a calibrated volumetric flask. A stopper was put on the flask and mixed. The contents was transferred into an appropriate glass container and labelled with the date prepared and concentration (10 µg/mL). The standard solution was stored in a refrigerator at 5°C.

Preparation of Working Standard Solution

From the stock standard, a working stock was prepared by transferring 1 mL of stock into a 50 mL calibrated volumetric flask and made up to the mark with methanol. A

stopper was put on the flask and mixed. The contents were transferred into an appropriate glass container with a label containing the date prepared and concentration (0.2 ng/µL) of the solution. The solution was stored in a refrigerator at 5°C.

Samples and calibration standards, verification standards and method blanks were decanted into the vials and sealed using a new septum each time to ensure proper sealing of the contents and minimisation of cross-contamination.

After loading the vials into the auto sampler, the external heating element was switched on to heat the purge vessel to 70°C. The analysis sequence was set up on the computer program. The MS was auto tuned as required. The split flow on the GC was set to 20 mL/min. The sample sequence was set up and started on the GC-MS computer. A calibration curve was generated by analysing spiked deionised water.

Calibration curves were accepted if the correlation coefficients were greater than or equal to 0.950. The calibration standards were prepared from a the 0.2 ng/µL working stock solution as indicated in **Table 3.7**, by adding to a volumetric flask and making up to the mark with deionised water.

Table 3.7 Geosmin ans 2-MIB Calibration Standards

Standard concentration (ng/L)	Volume of working stock added (µL)
Method Blank	0
10	50
20	100
30	150
40	200

Compounds were identified by matching both the retention times with that of the known standards. Quantification of compounds was carried out by means of the calibration curve generated.

3.5.18 E. Coli

Membrane filtration method – The samples were taken in a sterile glass bottles and filtered through 0.45um sterile membrane filters using sterilized membrane filtration equipment. The membrane filters were then placed on a petri dish containing selective growth media and incubated at 35 °C.[22]

3.5.18.1 Apparatus and Reagents

The following reagents and apparatus were used for the determination of E. Coli using the membrane filtration method: Readily prepared petri dishes containing chromocult coliform agar supplemented with E.Coli selective supplement; Sterile microbiological grade de-ionized/de-mineralised water; Clean, microbiology laboratory grade 1000 millimetre SCHOTT-DURAN bottles; Sterile 1000 microliter, 5 and 10 millimetre disposable plastic pipette tips; 100-1000 microliter, 1 to 5 and 5 to 10 millimetre pipette; and Sterile filtration flasks; Forceps with rounded tips for handling membranes; EZ-Pak membrane filter dispenser;

EZ-Pak Membrane filters of 47 mm diameter composed of cellulose esters, with filtration characteristics equivalent to a rated nominal pores diameter of 0.45 Micro meters and preferably with grids; A calibrated incubator capable of maintaining a temperature of 36 ± 1°C; A semi-automatic counter with a pen to mark the petri dish above the colonies connected to an electronic counter. A tangential light source and magnifier will aid viewing of the colonies on a small screen; A calibrated autoclave capable of reaching and maintaining a temperature of 121ºC ± 3°C for the entire sterilization cycle of 15 minutes at 15 psi of pressure.

3.5.18.2 Experimental Procedure

The filtration flasks were sterilised in the autoclave under the same conditions of operation, by using autoclave bags and putting multiple flasks

inside the bag. The autoclave tape was placed on the autoclave bag. After sterilisation, the flasks were removed from the autoclave and placed in the laminar flow cabinet to cool and dry.The work area was disinfected by wiping with 70% ethanol (i.e.7 parts ethanol: 3 parts distilled water of 99,9% ethanol).

The filtration unit was assembled by connecting the pump to the multiple filter holders with the water recovery glass container, gas flame, forceps, filter dispenser and everything required for the analyses in the work area to minimize unnecessary movement between analyses. If samples were refrigerated, the sampling bottles was removed from the fridge and placed on the bench until they reached room temperature prior to being analysed. If the prepared solidified agar plates were refrigerated, the plates were removed from the fridge and placed on the bench until they reached room temperature prior to being used.

Petri dishes were labelled with the sample identity; volume of sample filtered using a permanent marker. Forceps were disinfected by dipping the front end into a 99% ethanol and flaming using a gas flame, thereafter waiting for it to cool down. The sterile filter paper was dispensed from the packaging and placed on the filter holder using filter dispenser and sterile forceps.

After switching on the vacuum pump, the sample was mixed by inverting the sample 8 to 10 times in a uniform manner. The sample cap was opened and 100 mL of the mixed sample was transferred into the sterile flask. The valve on the filter holder was opened allowing water sample to filter. For samples suspected to have high counts, instead of making dilutions a small known volume was transferred into the flask with a volume of at least 10 ml of Ringers solution. A volume of less than 10 mL was considered too small to be filtered directly.

Following the filtration of the sample, the forceps were disinfected the same as before and the filter paper was removed from the funnel (Care was taken not to tear the filter paper when removing it from the funnel) and it was placed onto the petri dish containing agar that had been appropriately labelled. The filter paper was placed on the agar surface making sure that there were no bubbles between the surface and the filter paper. The plates were inverted and incubated at 36°C ± 1°C for 24 hours.

Calculation and reporting of results:

The number of colonies per 100 mL of sample was calculated by counting colonies on the surface of the filter paper. Depending on the microorganism analysed (between total coliform and E. coli), the colour of colonies were observed. Pink to red colonies represents Total coliforms while dark violet to dark blue colonies represents E. coli. If the small volume was used from samples expected to have high counts, the final calculation was made by conversion to 100 mL. Results for both Total coliforms and E. coli colonies were expressed using the following Equation.

$$CFU/100mL = \frac{no\ of\ colonies}{V\ of\ sample\ used}\ x\ 100 \qquad (3.4)$$

where

CFU/100 ml - the amount of colony forming units per 100 mL of sample;

No of colonies - the number of colonies counted from the filter paper after incubation;

V of the sample used - the volume of the sample that was used for analysis.

3.5.19 Cryptosporidium and Giardia

Analysis for Cryptosporidium and Giardia was outsourced and was only conducted on the raw water and final due to the high cost. The analysis was only undertaken once every three months to determine compliance. The immunofluorescence

method for giardia and cryptosporidium method (AWWA standard method 9711B) was used.[6]

3.5.20 Cyanobacteria Enumeration and Identification

3.5.20.1 Apparatus and Reagents

Homogenizer, used to break up loosely aggregated flocs like Microcystis to improve counting accuracy (The drawback of using this instrument is that once cyanobacterial colonies are broken up, it may be difficult to accurately identify species and even genera. This is optional for taxonomy labs, but if a homogenizer is not used, it is important to count more fields or strips.) Inverted light microscope; Centrifuge where the buckets can swing out 90º; Humidifier; Dispenser pipette (500 - 5 000 µL); Stage micrometer; Personal computer (PC) with standard spread sheet or SCS (scientific counting software) (This is optional, because other counting devices can also be used).

3.5.20.2 Experimental Procedure

Samples were fixed once they were received in the laboratory by adding Lugol's solution. The ratio of Lugol's solution added to a sample was 1:100 (the sample should be a weak tea colour). The sample was homogenized with a homogenizer to ensure an even distribution of cells aggregated in loose colonies (±20 seconds). The shaft was rinsed thoroughly with reagent water to prevent contamination of other samples. The sample was agitated before pipetting a known volume of sample (0.5 mL - 5 mL) into a sedimentation chamber (depending on the concentration of algal cells in the water). Separate pipette tips were used for each of the sample to prevent contamination. The sample was centrifuged inside the sedimentation chamber for 10 minutes at 3500 rpm. The centrifuge was balanced prior to commencement of the experiment. The sedimentation chamber was carefully removed from the centrifuge, making sure not to disturb the sedimented phytoplankton. If immediate analysis was not possible, the sedimented samples were placed in

a humidifier (filled with water at the bottom) to prevent evaporation. The sedimentation chamber was placed on the stage of an inverted light microscope. The 40x objective was used for analysis.

The algal genera present on the surface of the sedimentation chamber was identified and enumerated in random fields (one field is the area within the Whipple grid). A minimum of 60 fields were analysed per sample. Alternatively, analysis was stopped when at least 100 cells (of the dominant species) have been counted before 60 fields have been analysed. When only part of a cell was located within the Whipple grid, then it was counted only when more than half of the cell was within the grid and ignored if less than half of the cell was within the grid. Every algal cell was counted as one, whether it was part of a colony, filament or a single cell. Phytoplankton was identified to genus and/or species level with suitable taxonomic keys. Phytoplankton biomass was expressed as the amount of algal cells per millilitre (cells/mL).

3.6   References

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RESULTS AND DISCUSSION

4.1   Introduction

Data was gathered during a plant trial period of March 2015 to February 2016 to cover all seasons of the year in the southern hemisphere. Bench scale tests were also conducted during this period. A comparative analysis of the various oxidants (i.e. chlorine dioxide, chlorine gas and ozone) was carried out by using them in Plants 3, 2 and 1, respectively.

4.2   Chlorine Dioxide Concentration (Generated Product)

The chlorine dioxide generator was operated at a recommended pH of 3.5.[1] The generator displays a calculated theoretical concentration of chlorine dioxide in parts per million. The calculated chlorine dioxide concentration was verified by titration. An example of the titration results is shown in **Table 4.1**. The calculation of the different species in solution was undertaken according to Table 4.2. This particular example displays the chlorine dioxide generation data obtained for March 2015.

Table 4.1 Titration Data

Sodium Thiosulphate Conc. (N)		0.113	
Sample size		1	
Titrator Digits			
147	580	14	0
A	B	C	D
(digits / 800) / sample size			
0.1838	0.7250	0.0175	0.0000

Table 4.2 Titration Calculations

Species present in generated product	ppm

Chlorite, mg/L: D * N * 16,863.	0.00
Chlorine Dioxide, mg/L: (5/4) * (B - D) * N * 13,490	1381.46
Chlorine, mg/L: (A – [(B – D) / 4]) * N * 35,453	10.01
Generator Reading	1420
Generator Efficiency	97%

The calculated ClO_2 concentration on the generator was found to be 1420 ppm. A direct spectrophotometric reading was also done and a slightly higher ClO_2 concentration of 1482 ppm was obtained when this method was used. It should however be noted that the ClO_2 solution employed for the spectrophotometric method of analysis was diluted by 50% in order to accommodate the detection range of the instrument. The ClO_2 concentration was found to be 1310 ppm with no excess chlorite in solution and a slight excess of chlorine concentration of 10.01 ppm when the titration method was used.

The efficiency of the generation method was calculated using the actual and titration determined concentrations. The generator efficiency was excellent throughout the trial period and it varied between 96% and 98% (see **Figure 4.1**), which concurs with results obtained in previous studies using the two chemical method.[2]
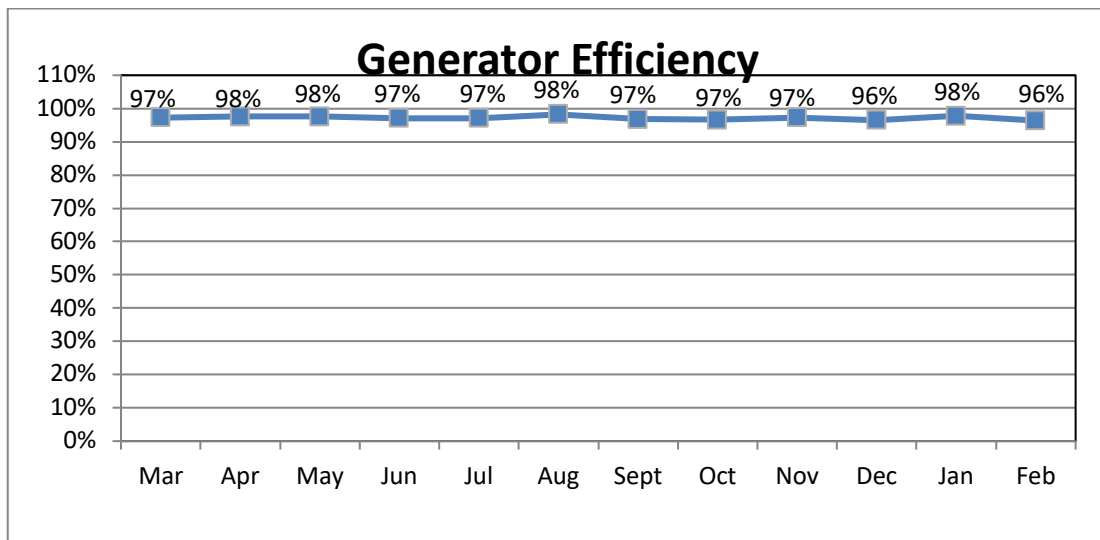
Figure 4.1: Efficiency of the Chlorine Dioxide Generation Method

The chlorine dioxide demand tests have revealed 1.0-1.4 ppm chlorine dioxide demand in the raw water (see **Figure 4.2**). Whilst a 0.2 ppm chlorine dioxide residual was maintained at the water treatment plant inlet, a chlorine dioxide dosage of 1.5

ppm ClO_2 was applied at the raw water pump station. It is evident from **Figure 4.2** that the ClO_2 oxidant demand generally increases leading to the summer season (i.e. from August to February) and peaks during the mid-summer month of January.
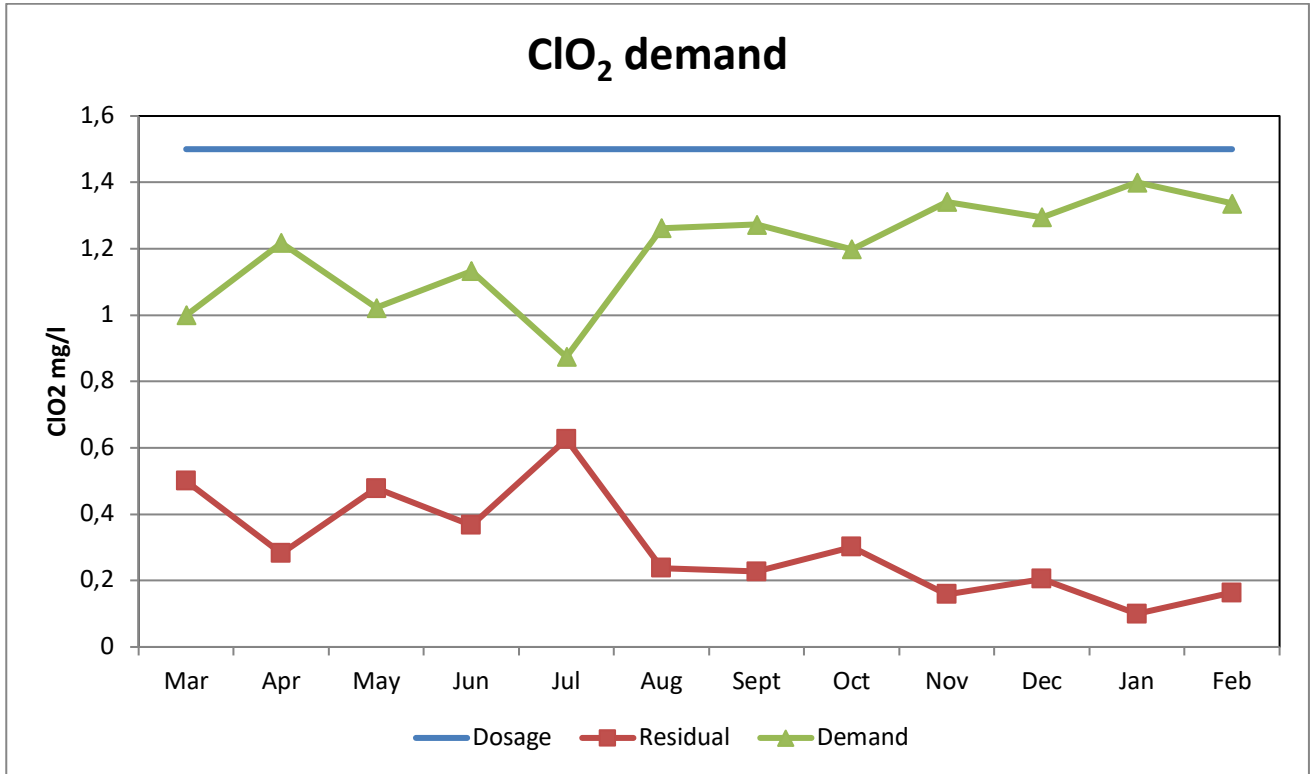
Figure 4.2: Raw Water Chlorine Dioxide Demand

4.3   Chlorine Dioxide Residual

Residuals of chlorine dioxide were measured from the inlet works (raw water after pre-treatment) and at the settling tank outlets and the results are displayed in **Figure 4.3**. The ClO_2 residual of between 0.2 ppm and 0.6 ppm was maintained at the inlet works. A significant drop in the chlorine dioxide residual was recorded for the month of April, which indicates an increase in the chlorine dioxide demand. The months of May, June and July showed an increase in the ClO_2 concentration of the raw water after pre-treatment and sedimentation outlet. This can be attributed to the lower temperatures, which lowers algal growth during this period, which causes a decrease in the oxidant demand and thus an increase in the residual.[3] The residual

ClO_2 concentrations gradually decreased again from August and remained relativity stable between 0.1 ppm and 0.2 ppm during the summer months September through February.
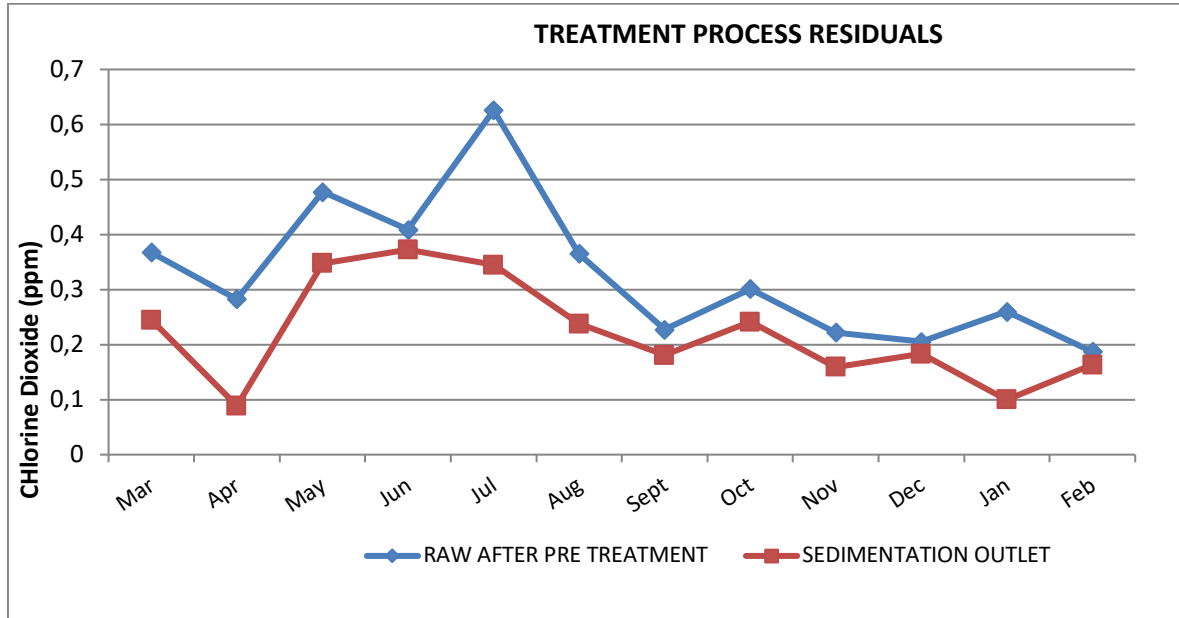
Figure 4.3: Measurements of Chlorine Dioxide Residuals

4.4 Jar Tests

4.4.1 Coagulant Demand

A comparative analysis of the jar tests conducted using ClO_2 and Cl_2 as pre-oxidants is illustrated in **Figure 4.4**, which shows the settled turbidity as a function of coagulant dose at 1ppm ClO_2 dosage. To determine the optimum coagulant dosage, the

pre-oxidant dosage was kept constant while the coagulant dosage was varied. However, the jar test experiments were repeated for each of the several concentrations of the pre-oxidant. This variation in the ClO_2 concentration seem to indicate an improvement in the flocculation up to a ClO_2 dosage of 1ppm; no flocculation enhancement was observed above 1 ppm ClO_2 dosage.

Coagulant dosage was found to reduce by approximately 2ppm when ClO_2 was used as pre-oxidant instead of chlorine gas.
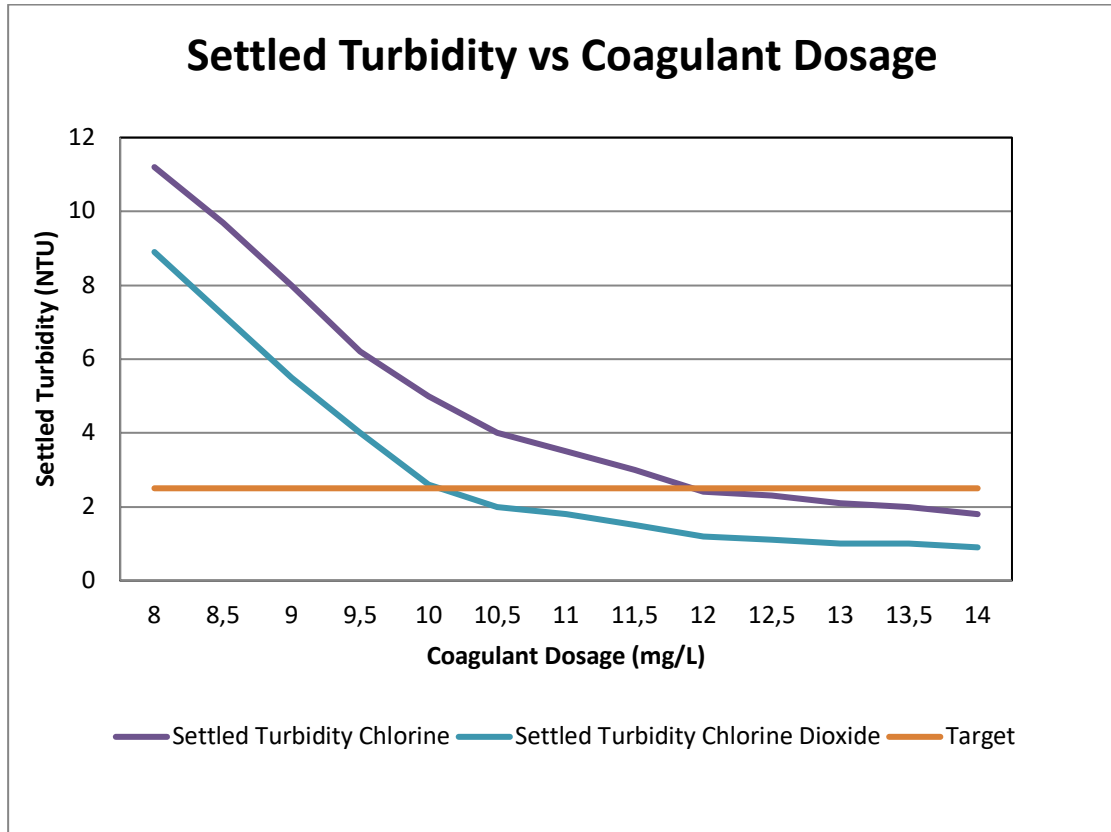
Figure 4.4: Coagulant Dosage with Different Pre-oxidants

4.4.2 Chlorophyll 665

The algal removal was determined at different concentrations of ClO_2. Algal enumeration is generally difficult to perform on samples that have been coagulated because the flocs obscure the view of the algae under the microscope.[4] It is for this reason that Chlorophyll 665 was adopted as an indicator for algal concentration. As shown in **Figure 4.5**, a significant reduction in the algal concentration (from 0.35 mg/L to practically zero) was observed when the ClO_2 dosage was increased up to an optimum level of about 2.0 mg/L.
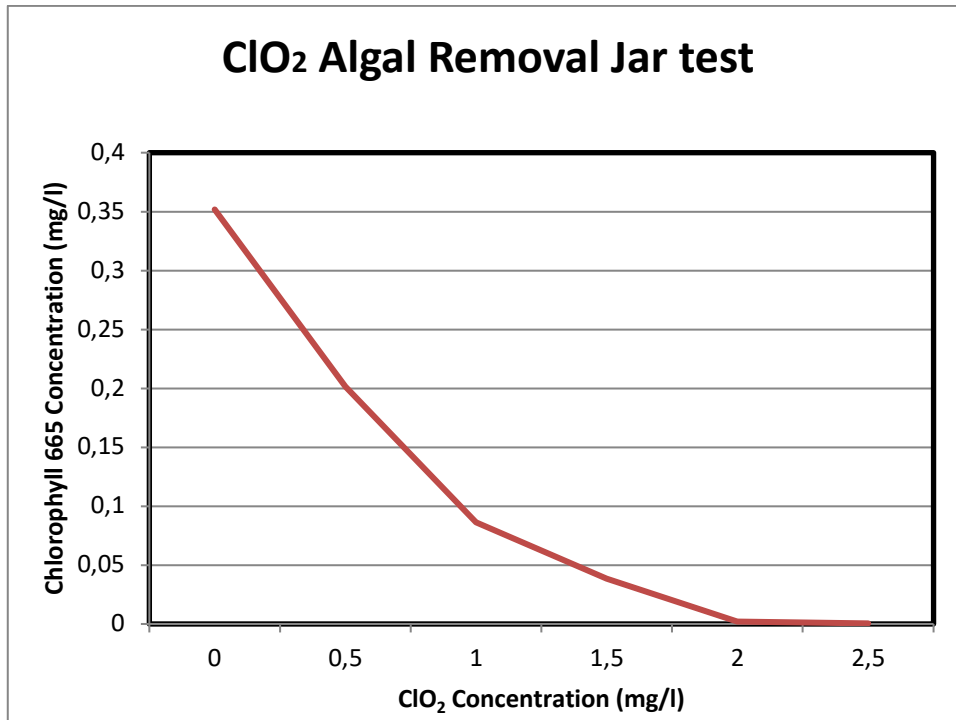
Figure 4.5: Algal Removal at Different Concentrations of ClO₂

4.4.3 Non-Organic Matter (NOM) Removal

The removal of NOM at different concentrations of ClO₂ was determined by varying the ClO₂ concentrations and using a constant and pre-determined optimum coagulant dosage for the prevailing raw water conditions. The results from the jar test, which are shown in **Figure 4.6**, indicate that the highest reduction in DOC (i.e. 15% removal) was obtained when a ClO₂ dosage of 0.5 ppm was applied. The calculated SUVA value for the raw water was below 1.5, which indicates the presence of low molecular weight NOM[5] of a hydrophilic character[6] that is typically difficult to remove with conventional water treatment processes.

The removal of the highly aromatic hydrophobic fractions of NOM (which are determined by UV_{254}) showed a similar trend as that of DOC removal (**Figure 4.7**). An optimum UV_{254} removal rate of 20% was achieved at a ClO₂ dosage of 0.5 ppm, and no significant increase in the removal of both DOC and UV_{254} was observed beyond this dosage.
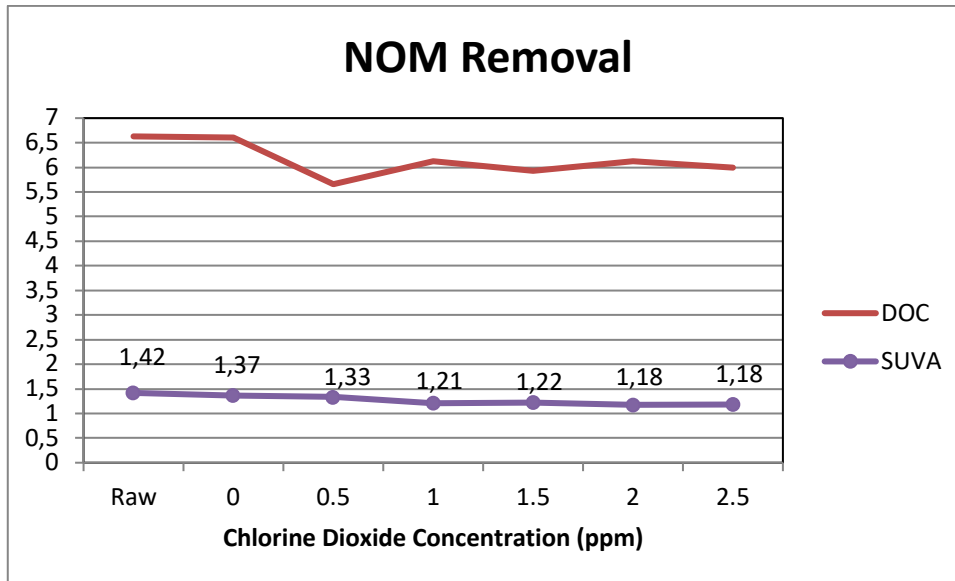
Figure 4.6: NOM removal at different ClO$_2$ concentrations
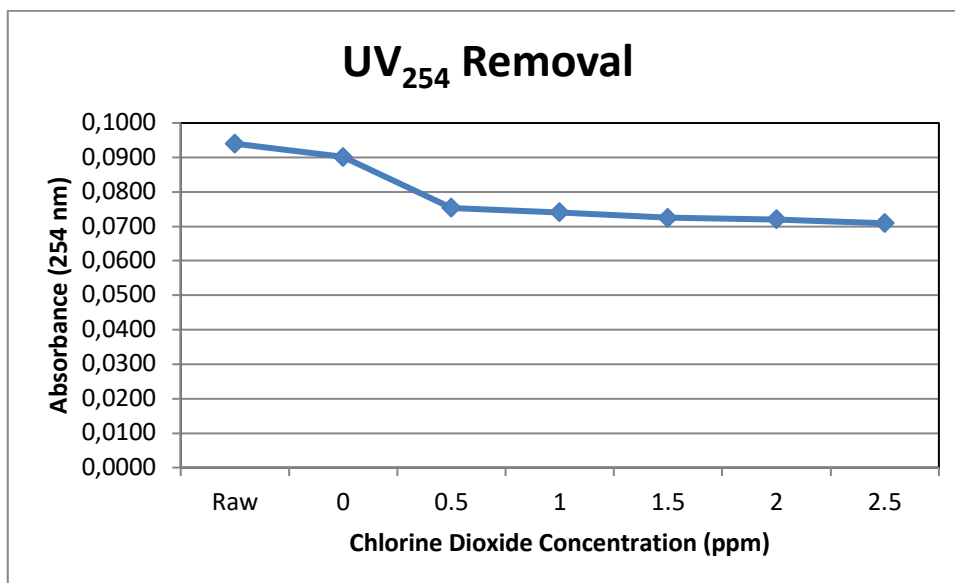
Figure 4.7: UV$_{254}$ removal at different ClO$_2$ concentrations

4.5   Determination of Plant Trial Parameters

4.5.1   Turbidity Measurements

The raw water turbidity was measured over a one year period and maximum turbidity of 43.7 NTU as recorded for the month of April 2015. Since no significant rainfall was experienced during this period, the spike in turbidity could be attributed to a temperature decrease brought about by a change in season,

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which may prompt a dam turnover (i.e. seasonal movement of water in a dam).[7] The raw water turbidity measurements over a one year period are depicted in **Figure 4.8**. A noticeable spike in turbidity during the mid-summer month of January 2016 (33.8 NTU), which is attributed to rainfall in the catchment causing an increase in raw water turbidity, was observed.
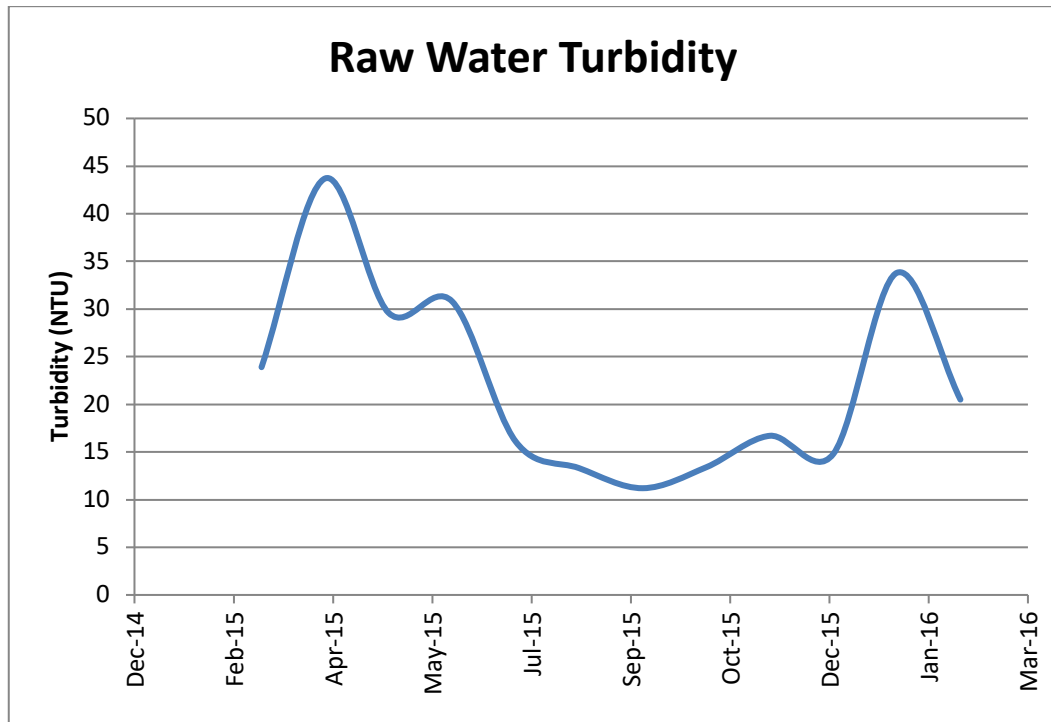
Figure 4.8: Seasonal Raw Water Turbidity

No noticeable difference in the final water turbidity was observed when ClO_2 (1.5 ppm) or Cl_2 (3.5 ppm) were used as pre-oxidants. The plants are continuously being optimized by process controllers to ensure compliance with SANS 241 and internal Magalies Water standards, which would eliminate any potential difference in performance efficiency when different pre-oxidants are used.

4.5.2   pH Measurements

The pH measurements of the raw water ranged between 8.1 and 8.9 from March 2015 to February 2016, with an average pH of 8.4 being recorded for this monitoring period. As illustrated in **Table 4.3**, the post pre-treatment pH for when

Cl_2 was used as a pre-oxidant (3.5 ppm) was found to be lower than that for ClO_2 (1.5 ppm). This could be attributed to the fact that, unlike chlorine which hydrolyses in water, chlorine dioxide remains dissolved as a gas in water.[8]

Table 4.3 pH Comparison Before and After Pre-treatment

pH	Min	Max	Avg
Raw	8.1	8.9	8.4
Raw after pre-treatment (Cl_2)	7.6	8.4	8.1
Raw after pre-treatment (ClO_2)	7.9	8.6	8.3

4.5.3   Electrical Conductivity Measurements

The conductivity of the different treatment process units when a ClO_2 dosage of 1.5 ppm was used was monitored during the period under investigation (see **Figure 4.9**).
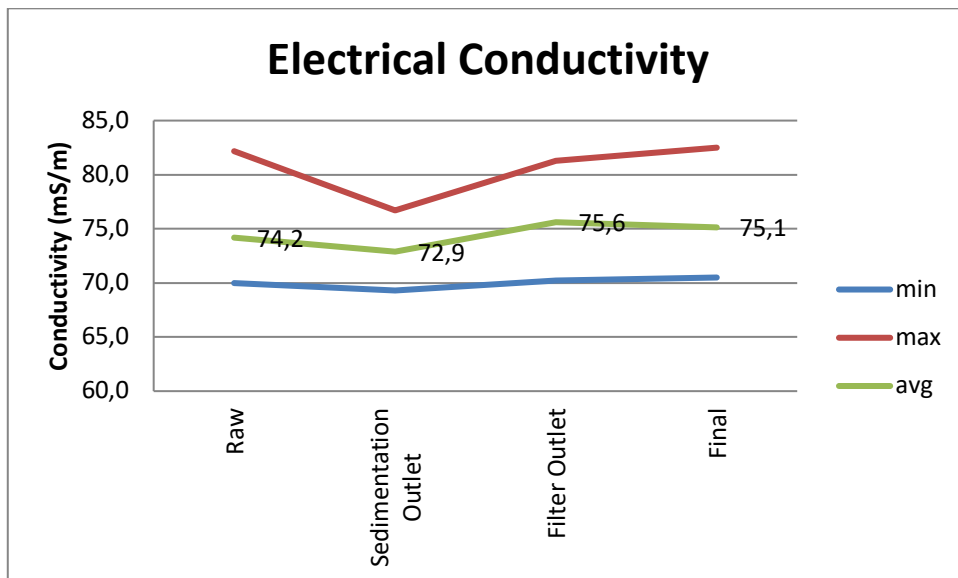
Figure 4.9: Process Train Conductivity

The raw water conductivity was found to range between 70 mS/m and 82 mS/m, which averages to 74 mS/m. The conductivity of the final water was found to be very similar (70.5 - 82.5 mS/m; average 75.1 mS/m). Although the conductivity

from the raw to sedimentation outlet was also similar (72.9 mS/m), a slight increase in the conductivity of the filter outlet (75.6 mS/m) and final waters (75.1 mS/m) was noted. No significant difference in the conductivity measurements of the raw and final waters was observed.

4.5.4 Dissolved Organic Carbon (DOC) Measurements

The DOC concentrations of the different treatment steps used in Plant 1 are shown in **Figure 4.10**. Ozone was used as pre-oxidant in the Plant 1 process train and the raw water DOC was found to be higher (10.1 ppm) than those of the other two plants (i.e. Plant 2 (8.3 ppm) and Plant 3 (8.3 ppm)). This can be attributed to the recycled water received by Plant 1 from the sludge dams. Despite the high in the raw water DOC levels, the highest DOC removal rate was still achieved for Plant 1.
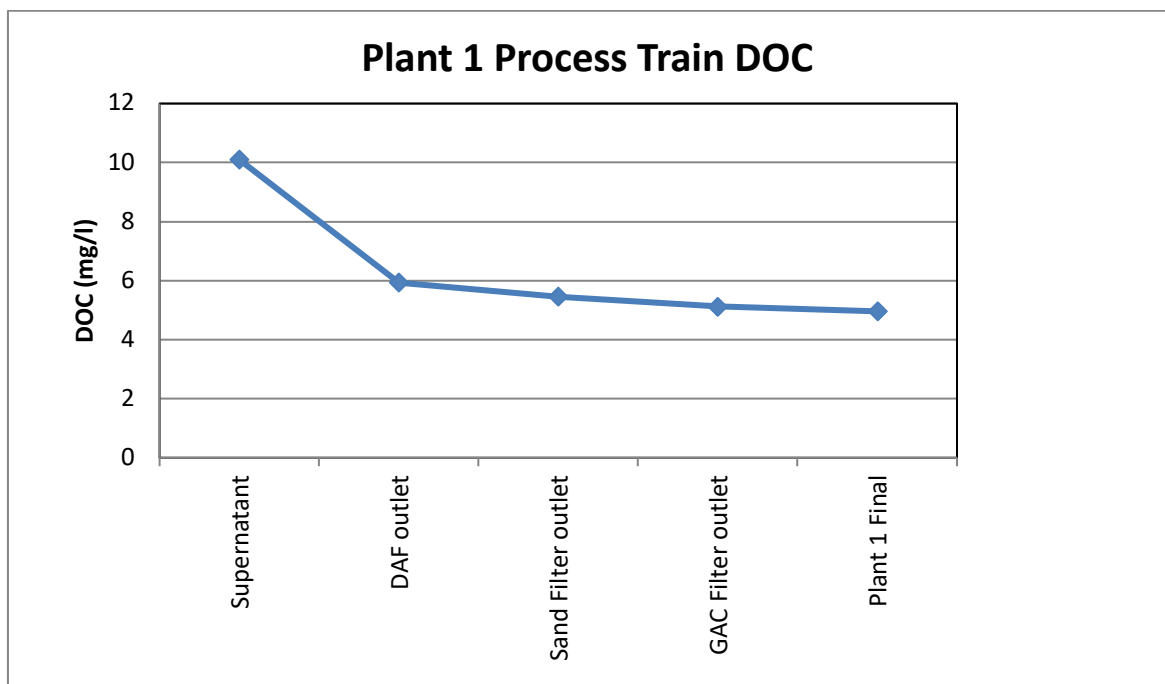
Figure 4.10: Plant 1 Process Train DOC Concentrations

The DOC removal rate for Plant 1 is presented in **Figure 4.11**. It can be seen that most of the DOC was removed (i.e. 41% removal) was achieved in the first

process (DAF) after the pre-treatment step. Overall, the DOC removal percentage for Plant 1 was found to be 50.9%.
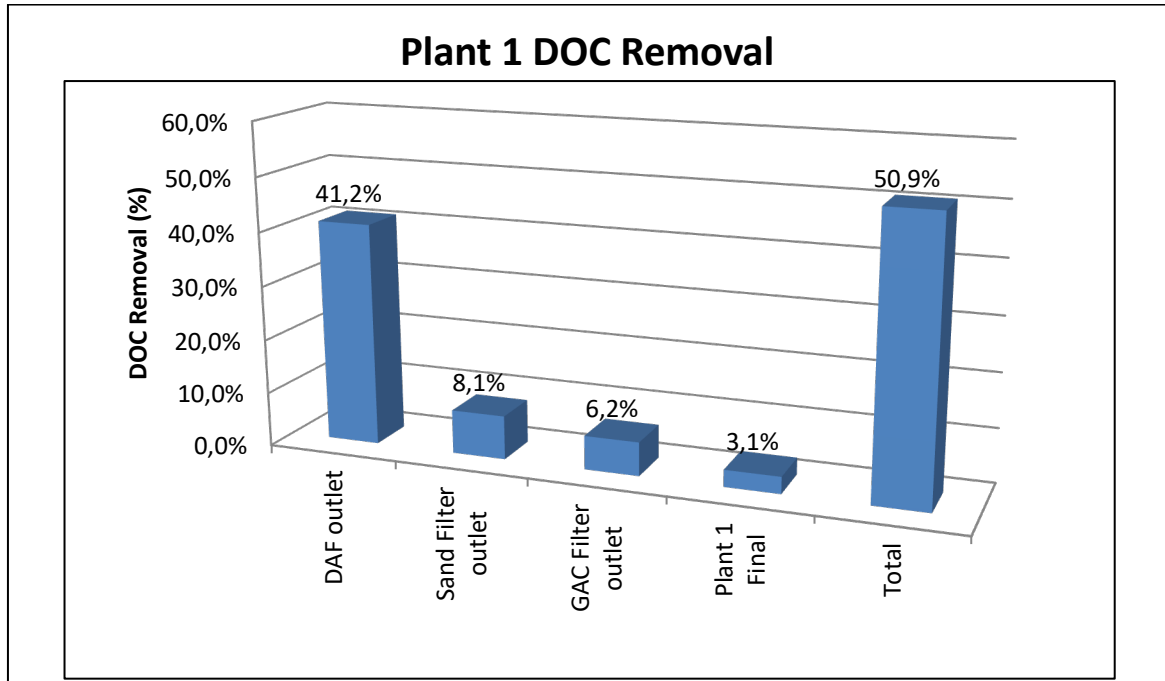
Figure 4.11: Plant 1 DOC Removal

The DOC concentrations of the various treatment steps involved in Plant 2 are reported in **Figure 4.12**. It should be borne in mind that chlorine was used as a pre-oxidant in the Plant 2 process train. It is evident from **Figure 4.12** that the DOC concentration was reduced significantly (from 8.3 ppm to 5.6 ppm) after the pre-oxidation step, and this concentration remained fairly constant in the rest of the unit processes.
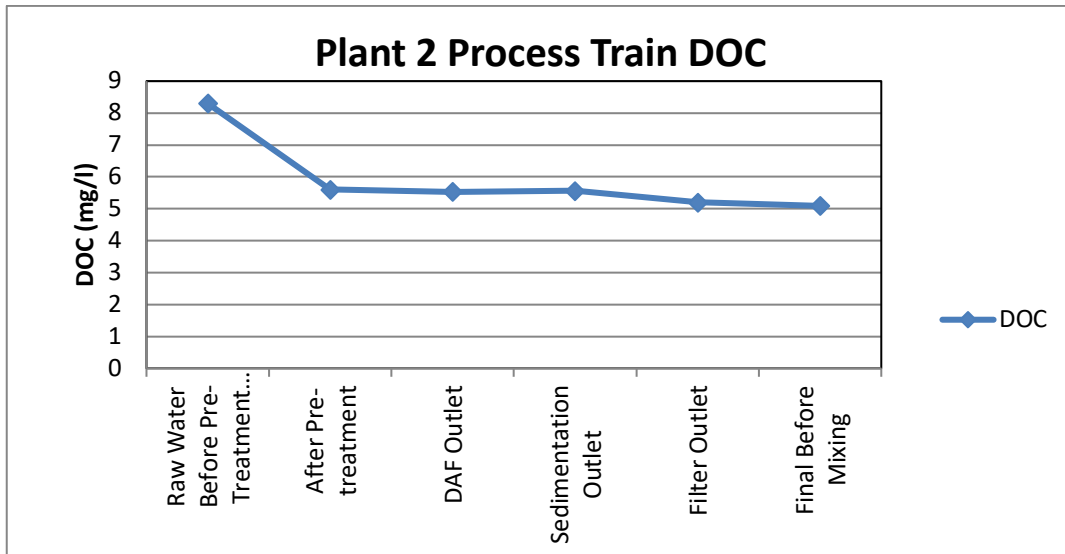
Figure 4.12: Plant 2 Process Train DOC Concentrations

A DOC removal percentage of 38.7% was achieved for Plant 2 Cl_2 was used as a pre-oxidant. As illustrated in **Figure 4.13**, most of this DOC removal (32.5%) occurred after the pre-treatment step.
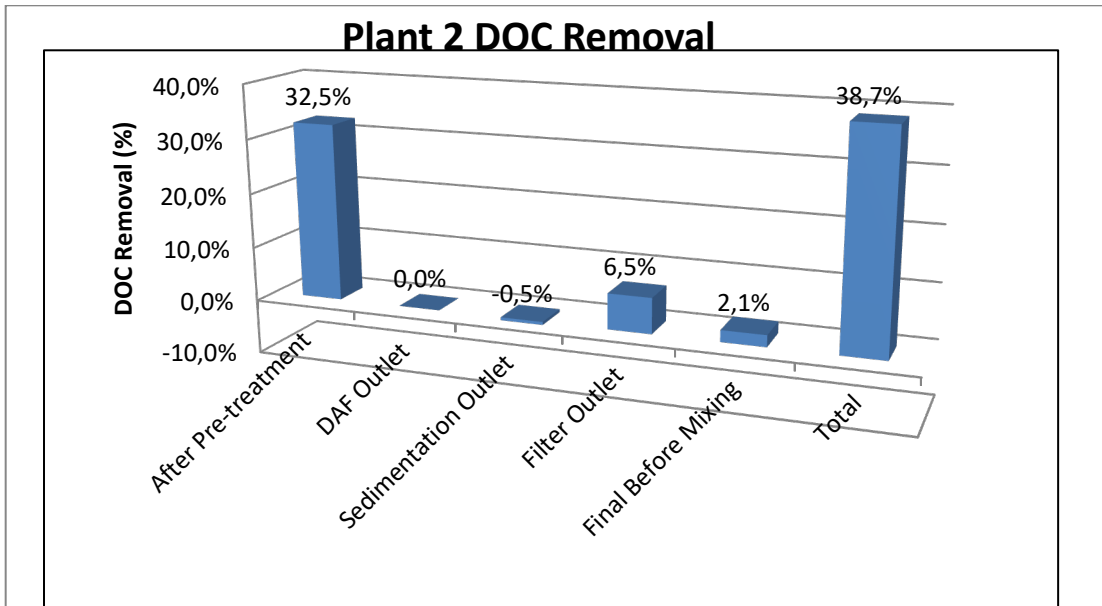
Figure 4.13: Plant 2 DOC Removal

Chlorine dioxide was used as pre-oxidant in the Plant 3 process train, and the DOC concentrations of the treatment steps for this plant are shown in **Figure 4.14**. As with the Plant 2 investigation, the DOC concentration was

reduced significantly (from 8.3 ppm to 4.72 ppm) following the pre-oxidation step and thereafter remained fairly constant (4.79 ppm and 4.32 ppm) for the rest of the unit processes.
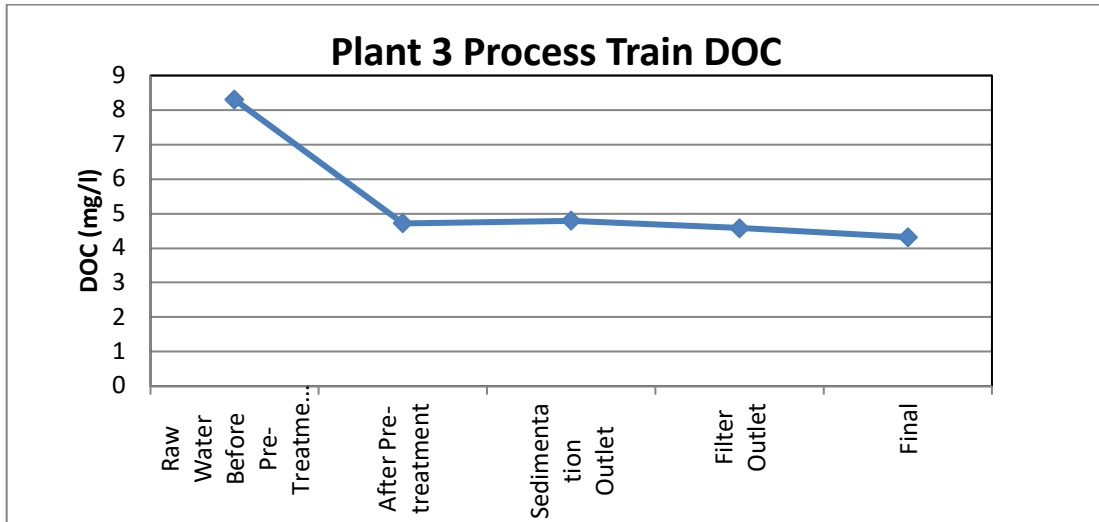
Figure 4.14: Plant 3 Process Train DOC Concentrations

DOC percentage removal levels very similar to Plant 2 were observed for Plant 3. In total, a removal percentage of 48% was attained. As illustrated in **Figure 4.15** and in line with results obtained for Plant 2, most of the removal (43%) was attained after the Plant 3 pre-treatment step.
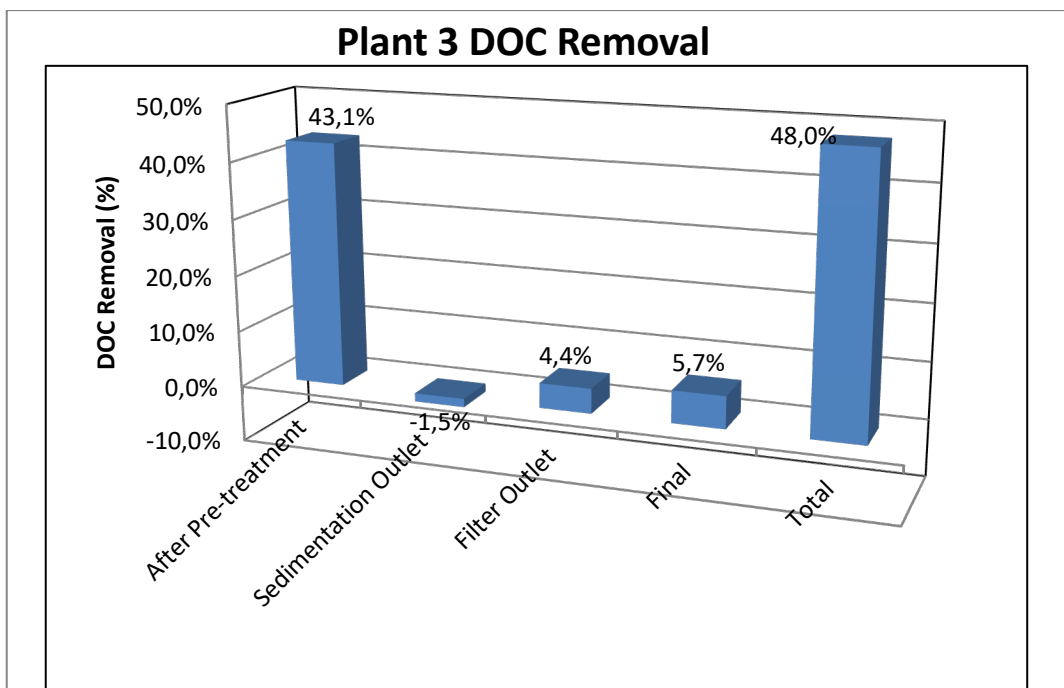
Figure 4.15: Plant 3 DOC Removal

4.5.5 UV$_{254}$ Measurements

The UV$_{254}$ values for the various raw water sources are shown in **Figure 4.16** and indicate that the highest UV$_{254}$ value (0.2809) was attained for the Plant 1 raw water. These results concur with the DOC results, which showed the Plant 1 raw water to possess the highest DOC concentration levels. The UV$_{254}$ values of both the filtered and unfiltered samples were determined, and the filtered samples were found to possess a lower UV$_{254}$ absorbance (0.1069) than the unfiltered samples (0.2368).
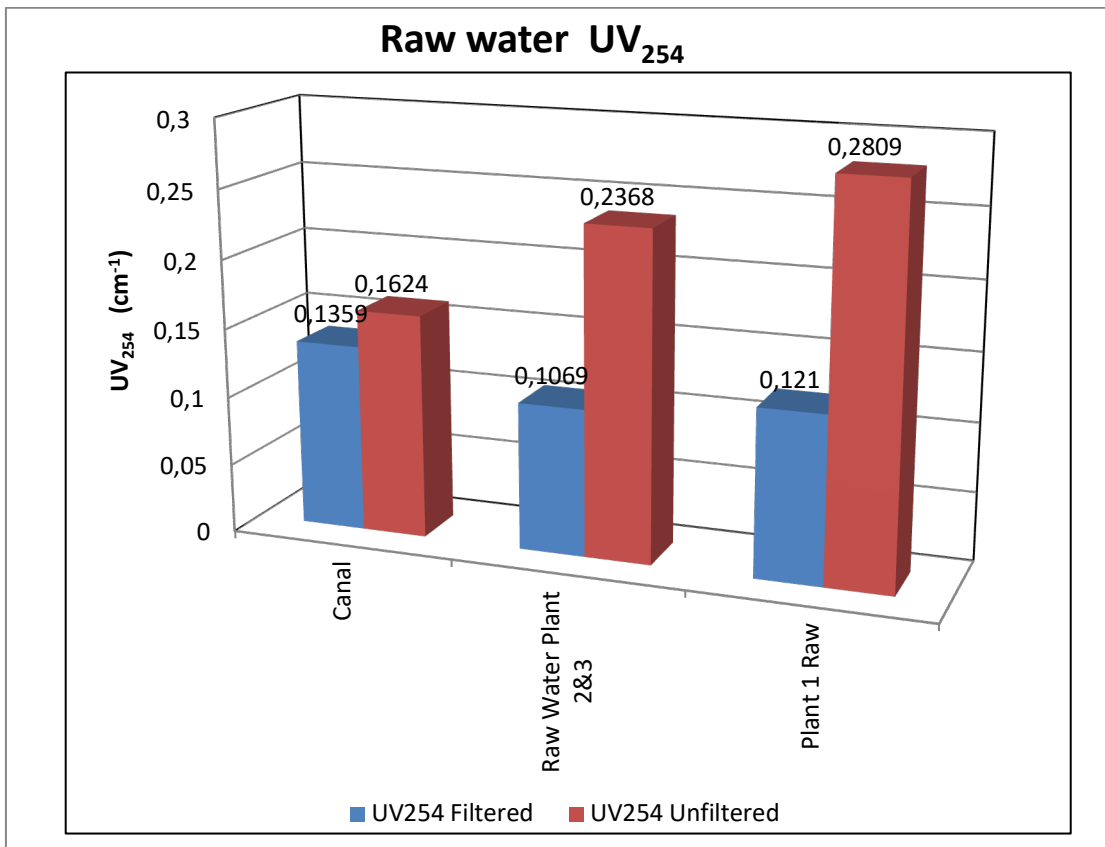
Figure 4.16: Raw Water UV$_{254}$

The Plant 1 UV$_{254}$ absorbance value was found to decrease throughout the different treatment steps. A lower UV$_{254}$ absorbance value was achieved for Plant 1 when ozone was used as a pre-treatment oxidant compared to chlorine. This is irrespective of the initial UV$_{254}$ absorbance value of the raw water being

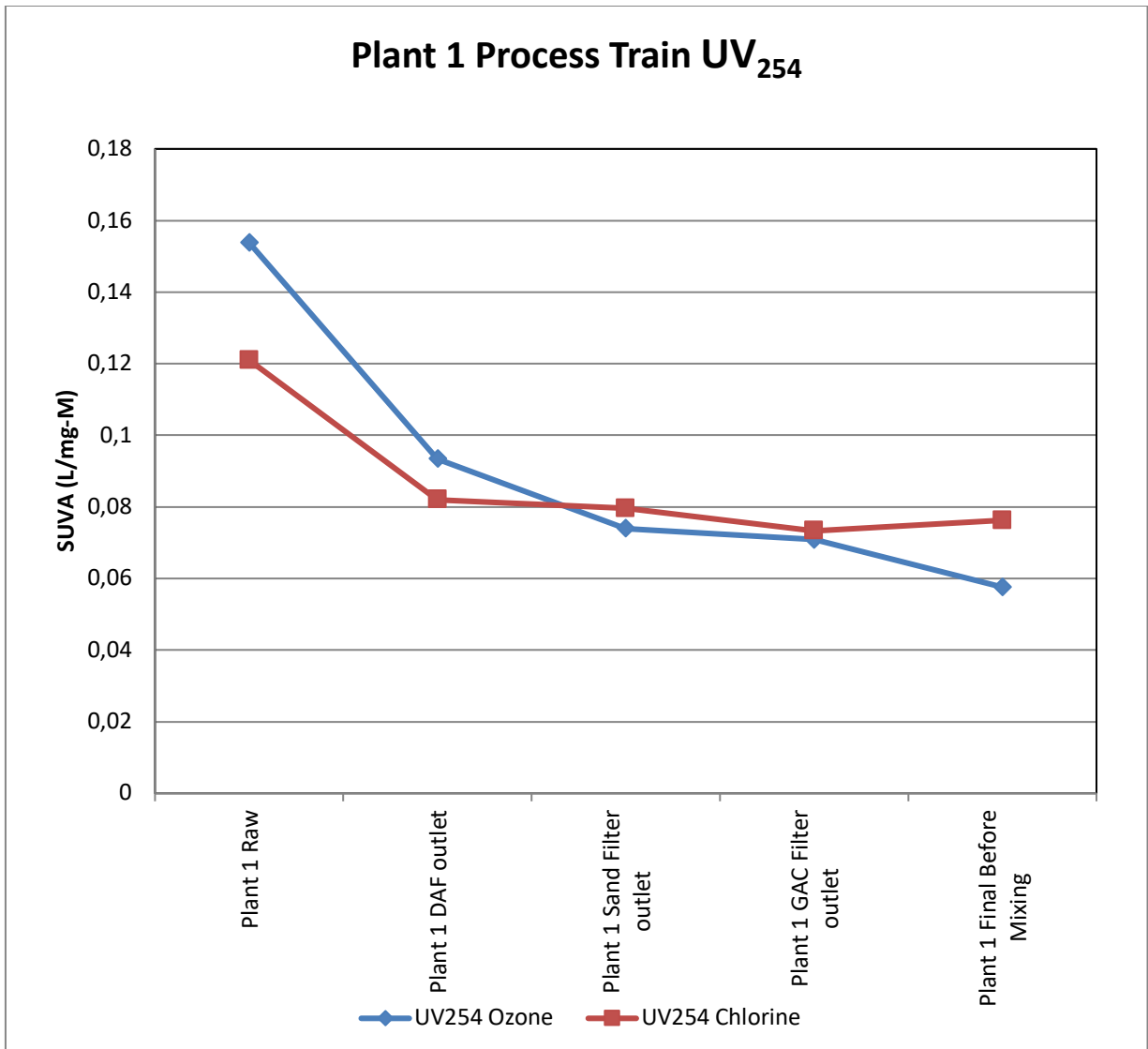higher than when the ozone was used as an oxidant (see **Figure 4.17)**.
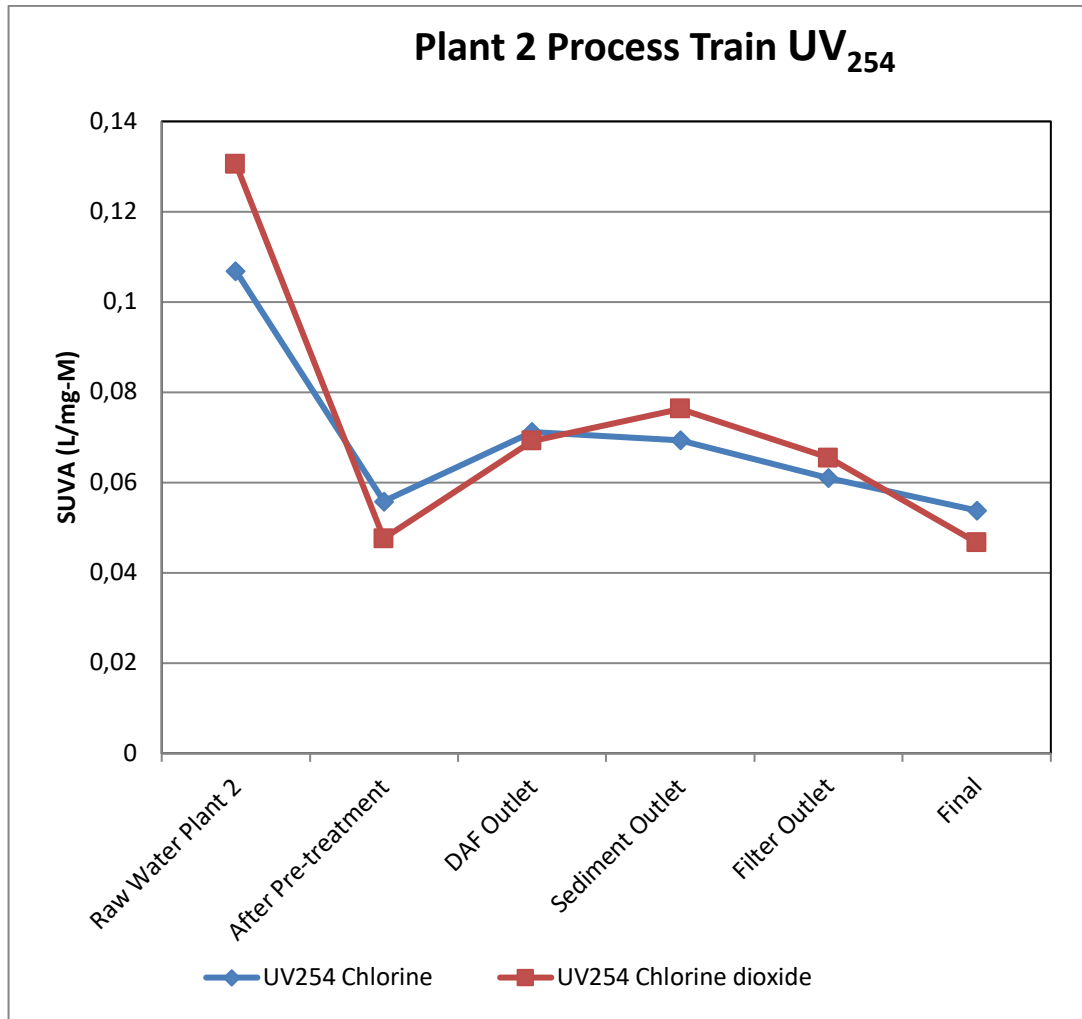

Figure 4.17: Plant 1 UV$_{254}$

As illustrated in **Figure 4.18**, the Plant 2 UV$_{254}$ absorbance value was also found to decrease from 0.1306 to 0.0467 during the different treatment steps. Plant 2 achieved a slightly lower UV$_{254}$ absorbance in the final (0.0467) water when using ClO$_2$ as pre-treatment oxidant compared to chlorine (0.0538), even though the initial UV$_{254}$ absorbance for the raw water was higher when the ClO$_2$ was used..

Figure 4.18: Plant 2 UV$_{254}$

The Plant 3 UV$_{254}$ absorbance value was also found to decrease from 0.1306 to 0.0466 during the different treatment steps (**Figure 4.19**). Compared to when chlorine was used as a pre-treatment oxidant, a lower UV$_{254}$ absorbance value (0.0466) compared to 0.0523 was achieved for the Plant 3 final water when ClO$_2$ was used as pre-treatment oxidant. This is despite the fact that the initial UV$_{254}$ absorbance value for the raw water was higher when the ClO$_2$ was used as an oxidant (0.1069 for chlorine and 0.1306 for ClO$_2$) .
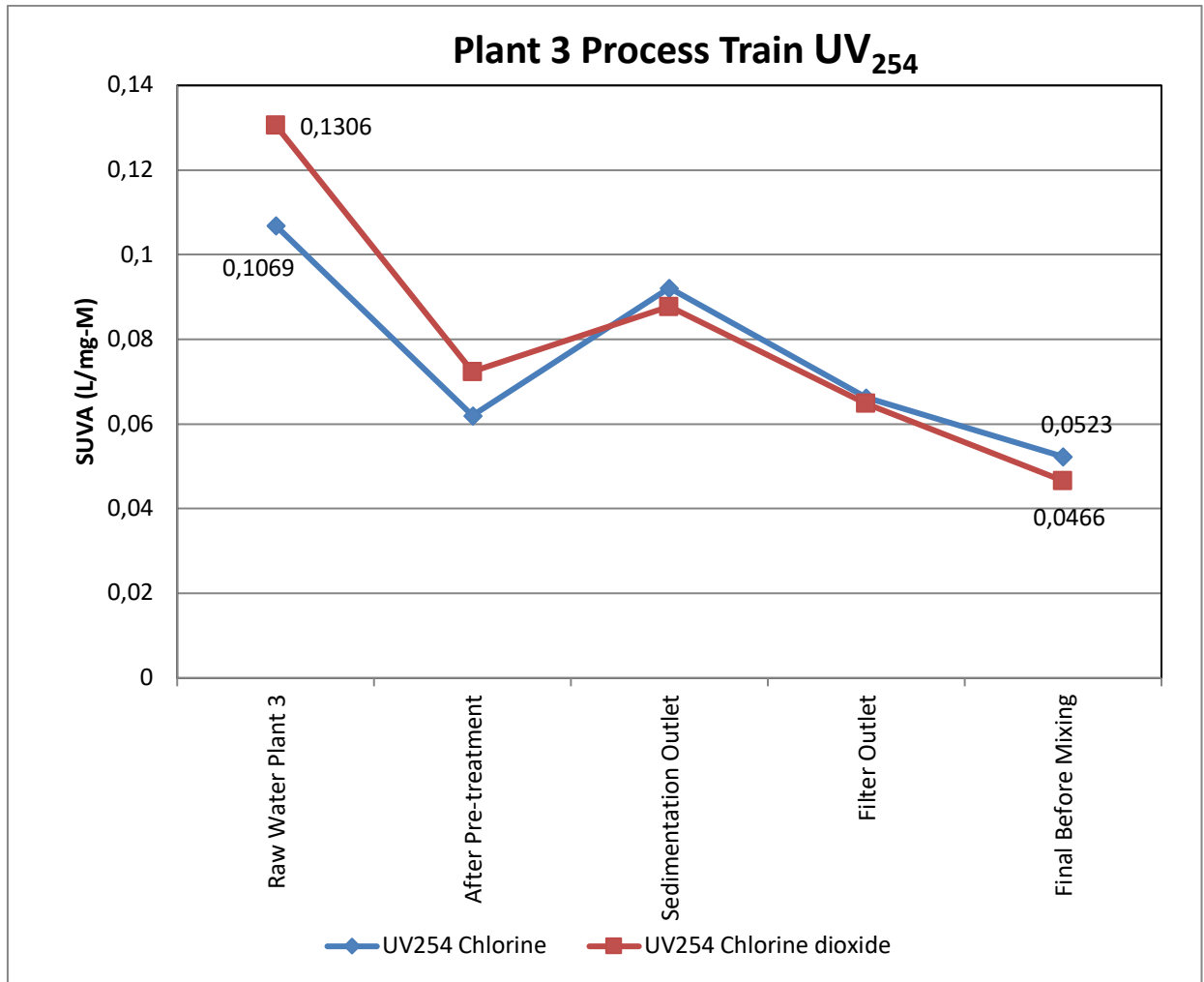
Figure 4.19: Plant 3 Process Train UV$_{254}$

4.6   Measurements of SUVA values

During the study it was established that the SUVA value of the raw water was below 2 (see **Figure 4.20**), which is indicative of the presence of a low moleclar weight NOM in the raw water. This type of NOM is basically the high fraction of non-humic matter with low hydrophobic character, which is typically difficult to remove by coagulation.[5]
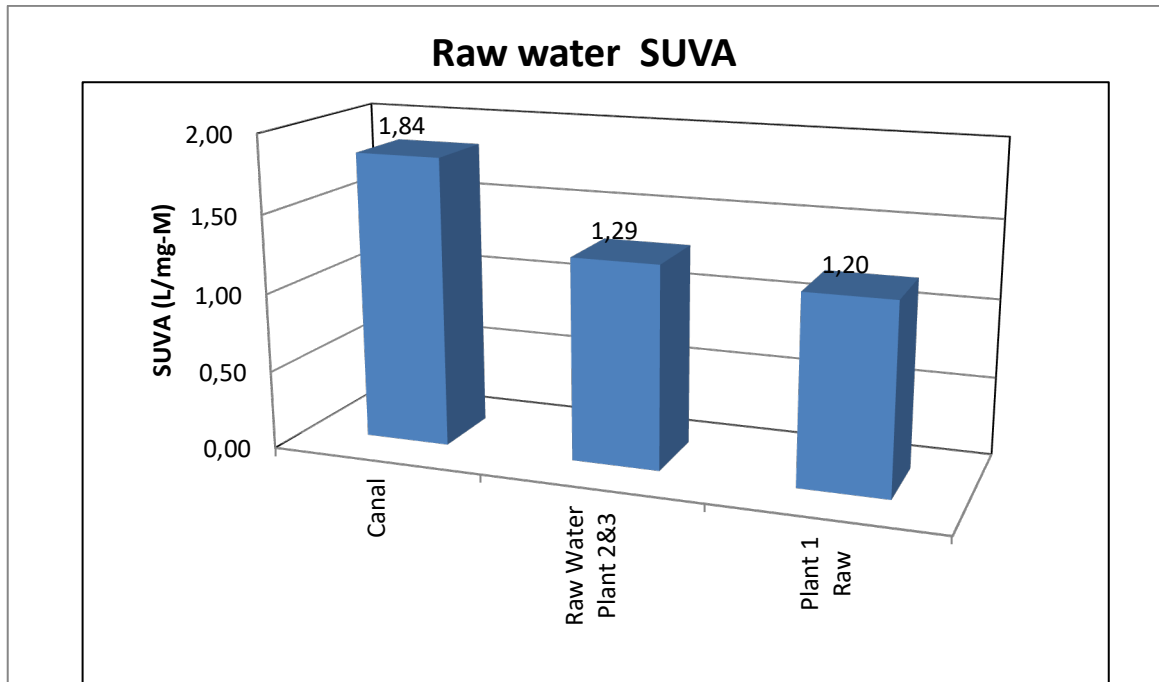
Figure 4.20: Raw Water SUVA

For ozone, the SUVA values were found to decrease during the various unit processes of the water treatment as compared to when chlorine was used as a pre-oxidant (**Figure 4.21**).
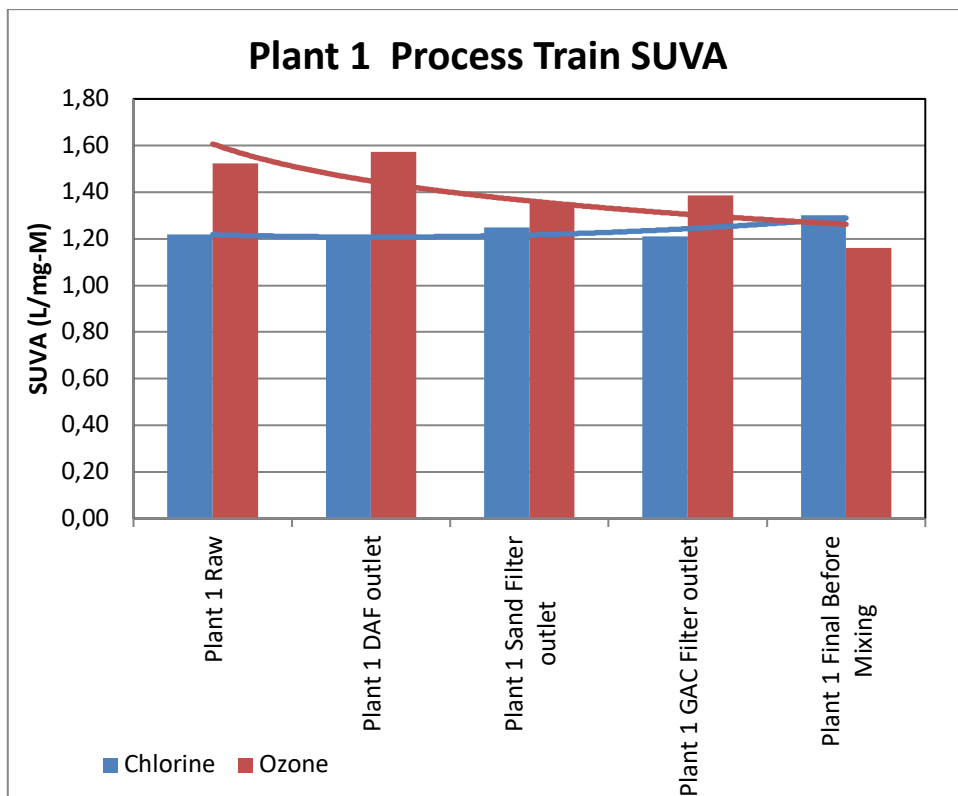

Figure 4.21: Plant 1 SUVA with Different Pre-oxidants

Results of an investigation of the effect of chlorine and ClO_2 pre-oxidants on the SUVA values of the Plant 2 process train are shown in **Figure 4.22**. The SUVA values for the Plant 2 raw and final waters are similar (1.29 for raw water; 1.28 for final water) when chlorine was used as pre-oxidant. A slight increase in the SUVA value (from 1.29 to 1.53) of the sedimentation process step was observed when chlorine was used as a pre-oxidant; the SUVA however remained the same for the raw and final waters. In contrast, the use of the ClO_2 pre-oxidant seems to have inspired a decrease in the SUVA values (from 1.57 to 1.11) of the respective raw to final waters.
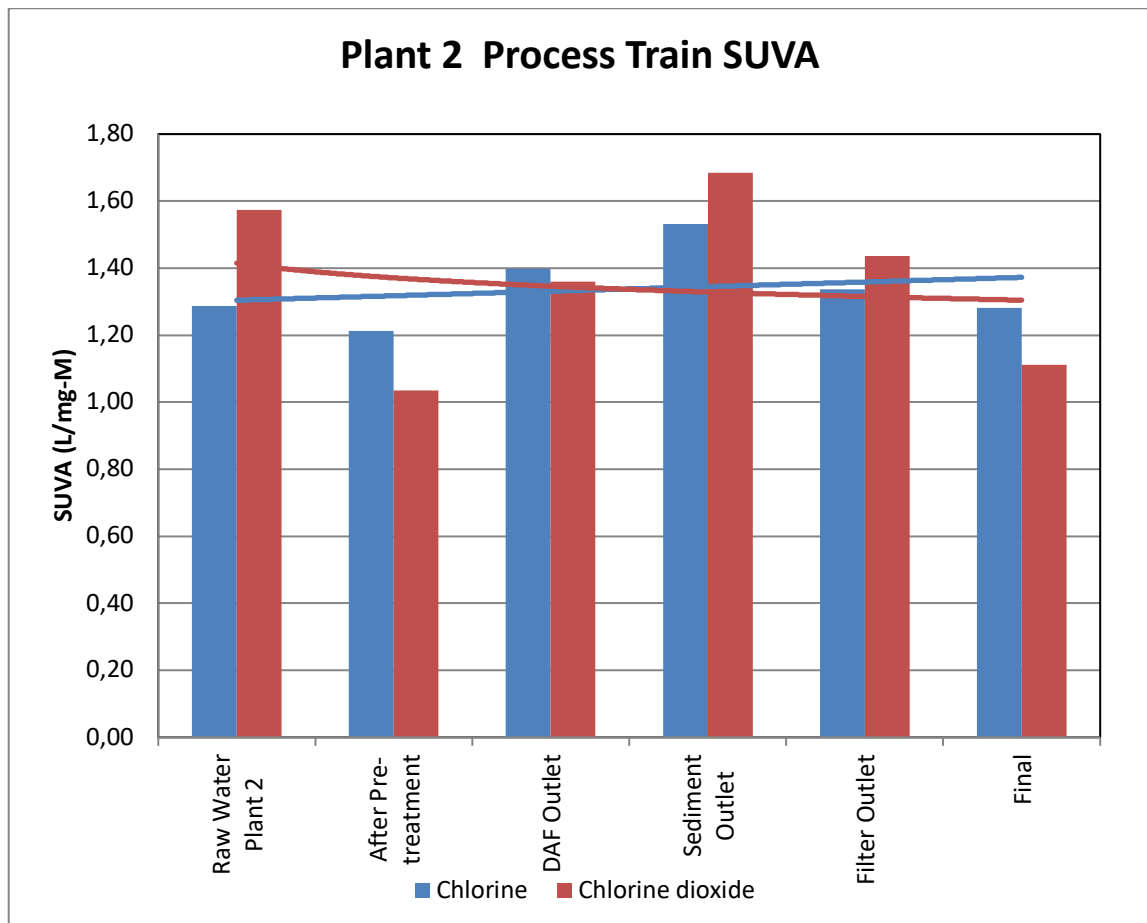

Figure 4.22: Plant 2 SUVA with Different Pre-oxidants

As illustrated in **Figure 4.23**, Plant 3 SUVA values followed a similar trend to those obtained for Plant 2. Once again the SUVA value was found to be relatively

high in the sedimentation step (1.92) but remained similar in the raw and final water when chlorine was used as a pre-oxidant. On the other hand, the SUVA value decreased when moving from raw water (1.57) to final water (1.08) with the use of ClO_2 pre-oxidant.
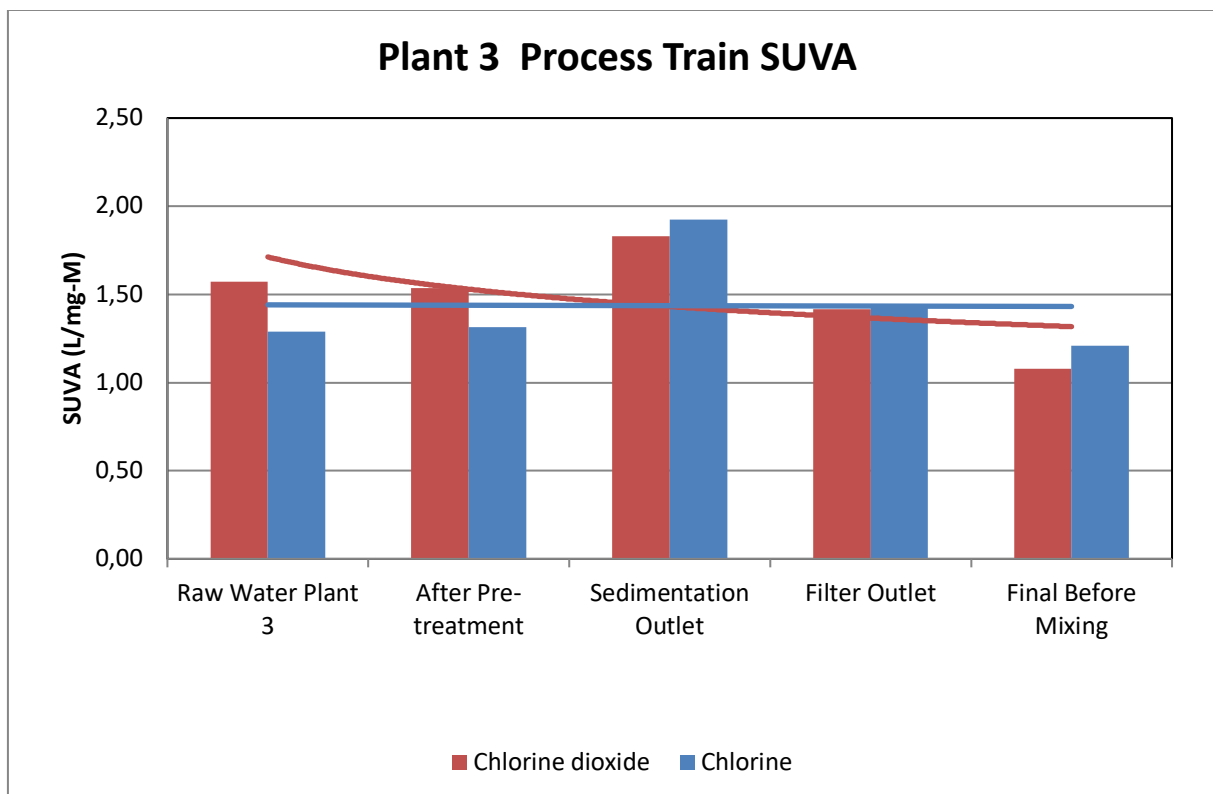
Plant 3 Process Train SUVA

Figure 4.23: Plant 3 SUVA with Different Pre-oxidants

4.7   Fluorescence Excitation Emission Matrices (FEEM) Analysis

FEEM of process samples was determined where chlorine dioxide and chlorine gas was used as pre-oxidants respectively. The matrix for the raw water sample is displayed in **Figure 4.24**. The matrices for the samples taken after the pre-oxidation, sedimentation and filtration steps for Plant 3 whereby chlorine dioxide was used as pre-oxidant are shown in **Figures 4.25**, **4.26** and **4.27**, respectively. The matrices for the samples taken after the pre-oxidation, sedimentation and filtration steps for Plant 2 when chlorine gas was used as pre-oxidant are shown in **Figures 4.29**, **4.30** and **4.31**, respectively. The raw water matrix was included in **Figure 4.28** for comparative purposes. The after pre-oxidation matrix when ClO_2 was used as a pre-

oxidant shows a much better removal efficiency of the humic-like NOM compared to when Cl_2 was used as an oxidant This is evident from the lower intensity of excitation above 350 nm on the ClO_2 matrix when compared to the Cl_2 matrix[9].
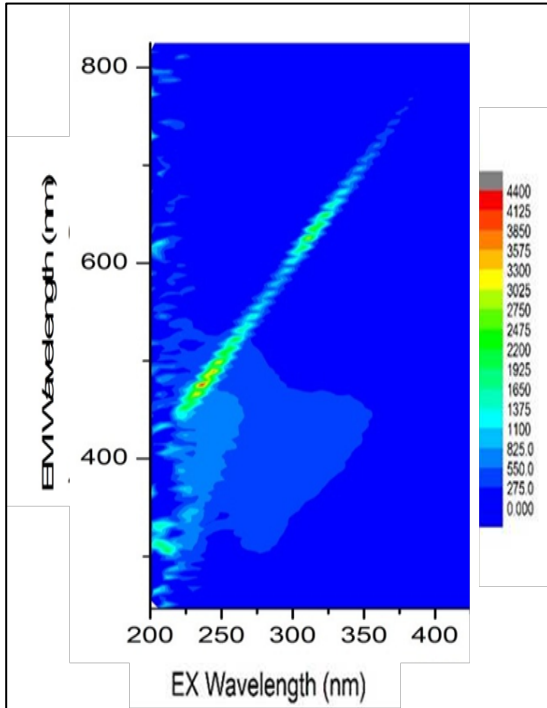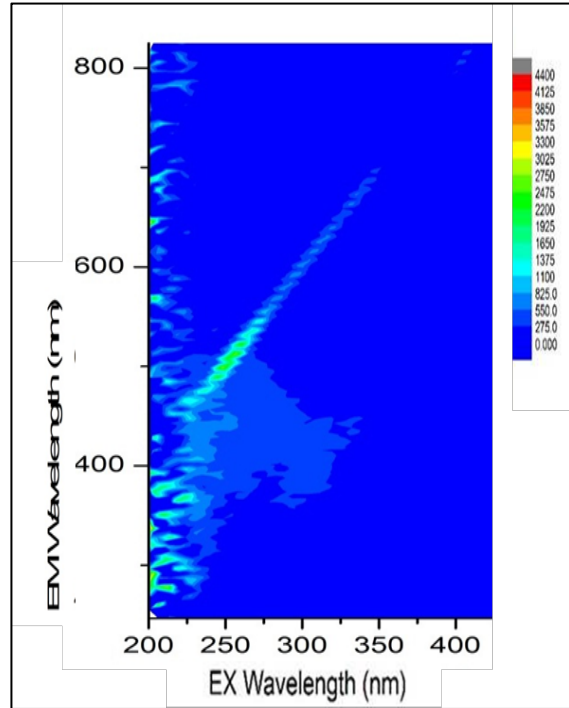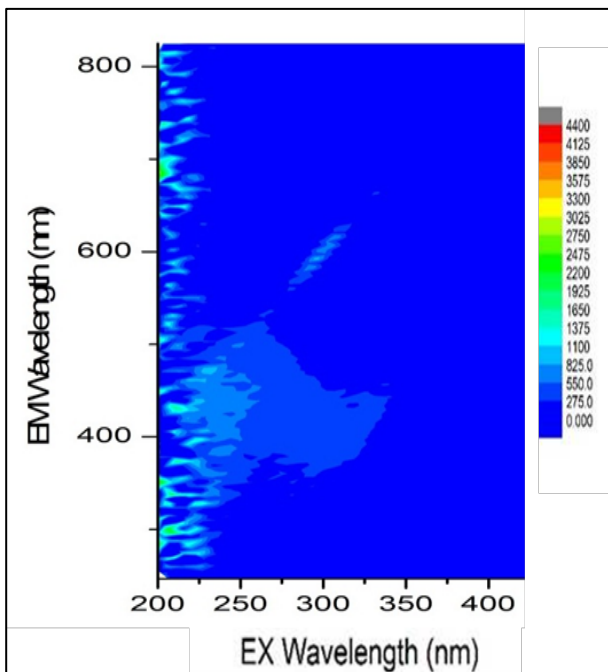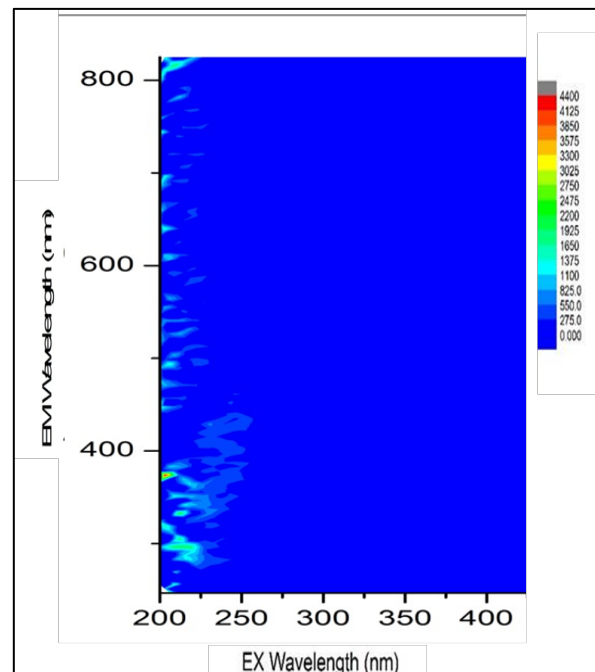

Figure 4.24 Raw water FEEM

Figure 4.25 FEEM After Pre-Oxidation ClO₂

Figure 4.26 FEEM After Sedimentation ClO₂

Figure 4.27 FEEM After Filtration ClO₂
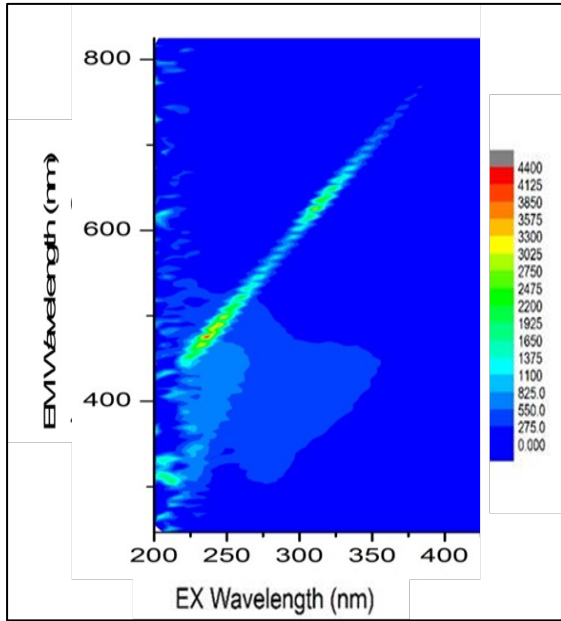
Figure 4.28 Raw Water FEEM Cl$_2$
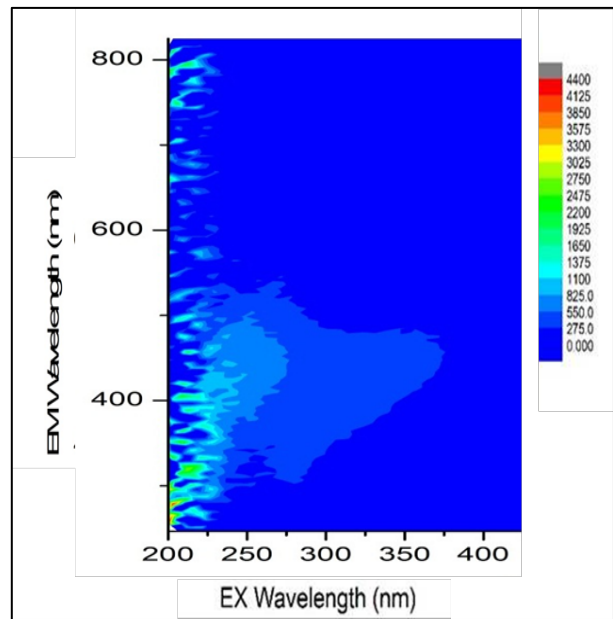
Figure 4.29 FEEM After Pre-Oxidation Cl$_2$
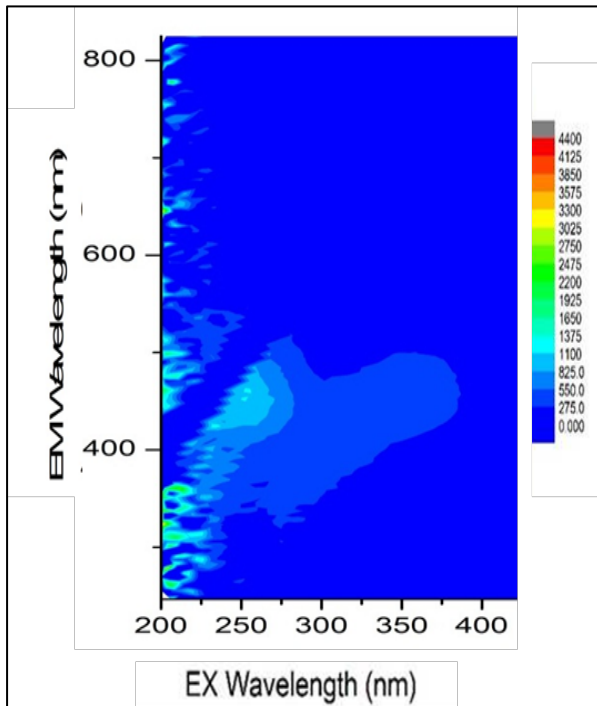
Figure 4.30 FEEM After Sedimentation Cl$_2$
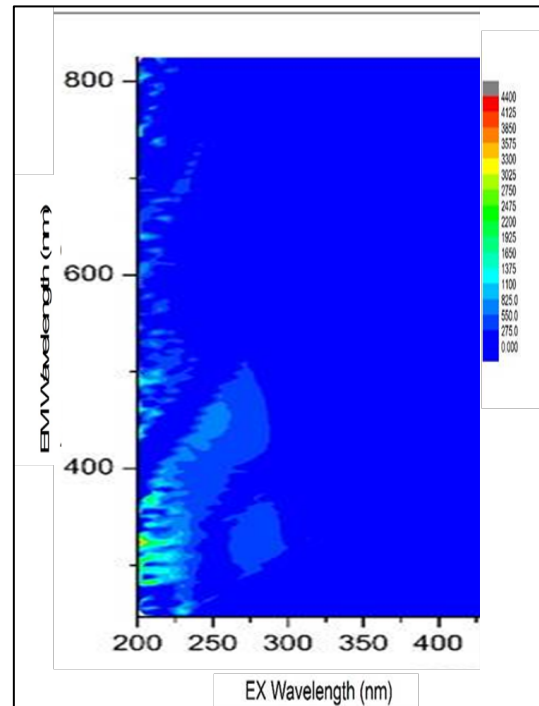
Figure 4.31 FEEM After Filtration Cl$_2$

The matrixes of the samples from the process train for ClO$_2$ shows a progressive reduced excitation and emission intensity and the range where the tyrosine, tryptophan and protein-like NOM emits shows a lower intensity than those for the

Cl$_2$ matrixes. A comparison between the samples from the filter outlets (**Figure 4.27** and **Figure 4.31**) shows a cleaner matrix, and thus better removal of NOM for ClO$_2$ compared to Cl$_2$.

4.8 Measurement of Iron and Manganese Concentrations

Measurement of iron and manganese in the raw and final water is of importance because of the potential of color formation in the final water when high concentrations of iron and manganese are present.[5] Elevated levels of manganese can cause a black to brown color[10] while high levels of iron can cause reddish brown color.[5] The iron and manganese concentrations in the raw and final water samples following ClO$_2$ pre-oxidation are shown in **Figures 4.32** and **4.33**, respectively. The raw water concentration for iron started increasing from April and reached a high in June (680 µg/L). In August the concentration dropped to below the SANS 241 aesthetic standard (≤300 µg/L) and reached a low in October (10 µg/L). The manganese concentration followed a similar trend but only started increasing from the month of May and reached a peak in July (159 µg/L) where after it decreased again in August to below the SANS 241 aesthetic standard (≤100 µg/L). There was a slight increase in September from 40 µg/L to 81 µg/L where after the concentration remained fairly constant between 80 µg/L and 100 µg/L
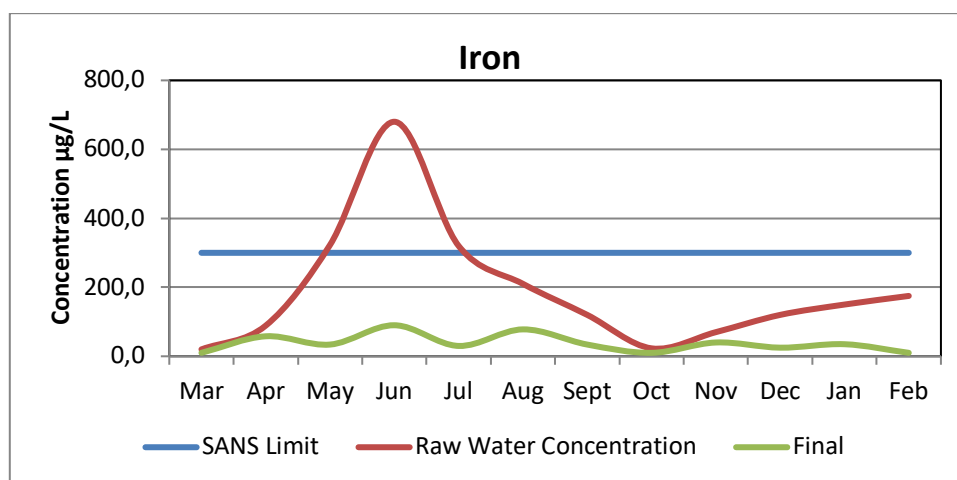
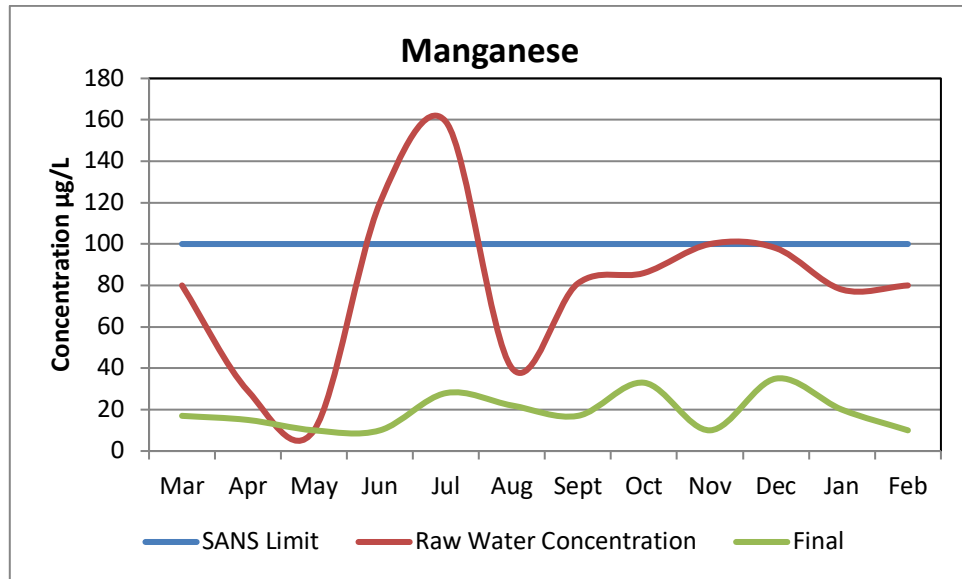

Figure 4.32 Iron Concentrations

Figure 4.33 Manganese Concentrations

The increase in the concentrations of both the iron and manganese can be attributed to dam turn over, similar to what was observed with the turbidities of the raw water.[7]

The analytical results of the final water reveal that enough removal of iron and manganese concentrations during the treatment process is achieved to obtain final water concentrations below the SANS aesthetic health standard (≤300 Fe and ≤100 Mn)[11]. The unit process results obtained at the outlet of the sedimentation tank were at similar levels to those obtained in the final water for both the iron and manganese. It can therefore be concluded that most of the iron and manganese was removed during the coagulation and sedimentation steps. This suggests that oxidation of the metals (Fe and Mn) and their subsequent removal by co-precipitation at the bottom of the sedimentation tank have indeed occurred.

4.9   Measurements of Trihalomethane (THM) Concentrations

The use of pre-oxidants (i.e. ClO2 or Cl2) in the water treatment process is often accompanied by the formation of disinfection by-products such as THMs. Typical THMs that are produced include bromoform, chloroform, dichloromethane and bromodichloromethane. Since these THMs are known to be carcinogenic, it is

important that their concentrations in water are monitored. To this end, concentrations of the THMs in the final raw water were determined and results for the two pre-oxidants are reported and compared in **Table 4.4**. The disinfection by-product formation when using chlorine gas and chlorine dioxide was compared.

Although the use of chlorine was accompanied by elevated levels of chloroform (0.22 mg/L) in the final water, such concentrations were still within the SANS requirements of ≤0.300 mg/L. The concentration of dibromochloromethane was also found to be high (0.09 mg/L) and did not comply with the SANS 241 standard (≤0.060 mg/L). Not only were low levels of THMs detected in the raw samples when ClO_2 was used as a pre-oxidant, these levels were found to be in compliance with the SANS 241 standard for the reporting period. It can therefore be concluded that the concentrations of THMs produced when chlorine was used as a pre-oxidant were generally much higher than those produced for chlorine dioxide. In some instances, the THMs produced from chlorine did not meet the statutory regulatory requirements of SANS.

Table 4.4. THM Species in Final Water

THMs	Concn levels (mg/l); Cl_2 as pre-oxidant	Standard deviation	Concn levels (mg/l) ClO_2 as pre-oxidant	Standard deviation	SANS 241 Requirements (mg/l)
Bromoform	0.01	0.003	0.01	0.002	≤0.100
Chloroform	0.22	0.06	0.01	0.01	≤0.300
Dibromochloro methane	0.03	0.02	0.01	0.01	≤0.100
Bromodichloro methane	0.09	0.03	0.01	0.01	≤0.060

4.10   Concentration Measurements of Geosmin and 2-MIB

The geosmin and 2-MIB concentrations were measured during the period of high algal concentrations due to the greater probability of detecting these algal metabolites during algal blooms.[12] The results are indicated in **Table 4.5**. Concentrations of geosmin and 2-MIB were found to be below 10 ng/L and 15 ng/L, respectively. This was despite the presence of very high concentrations of oscillatoria algae in the raw water, which is known to generate 2-MIB.[12]

Table 4.5 Geosmin and 2-MIB Concentrations

	Vaalkop Raw	Vaalkop Final	Vaalkop Raw	Vaalkop Final
Date	Geosmin		2MIB	
Aug-15	4.4	5.9	13	12
Sep-15	4.4	5	8.7	14
Oct-15	2.5	2.8	3.7	9.2
Nov-15	3.7	5.8	5	14
Dec-15	14	15	8	12
Jan-16	3.1	4.6	3.8	7.1

It is evident from this study the algal blooms did not give rise to any significant amounts of the geosmin and 2-MIB. This, therefore, implies that the algal bloom did not make any meaningful contribution to taste and odour problems in the water.

4.11   Taste and Odour Determination

No taste and odour problems were recorded during the trial period when chlorine dioxide was used as a pre-oxidant. This is despite the presence of high concentrations of taste- and odour-causing algae in the raw water (as indicated in **section 4.15**). There was thus a potential for the formation of taste and odour causing compounds such as geosmin and 2-MIB, however, these concentrations remained below the threshold limit of 30 ng/l.[12] When chlorine dioxide was stopped during December 2015, an immediate objectionable taste and odour in the final water became noticeable despite the presence of low concentrations of geosmin and 2-MIB (**Table 4.6**). This observation has led has led to a conclusion that the

taste and odour originates from a different source and not from geosmin and 2-MIB as previously suspected. Lastly, results presented in this section also show that chlorine dioxide was effective in the removal of the taste and odour compounds originating from sources other than geosmin and 2-MIB.

Table 4.6 Taste and Odour Rating

Month	Mar'15	Apr'15	May'15	Jun'15	Jul'15	Aug'15	Sept'15	Oct'15	Nov,15	Dec'15
Rating scale Taste	3	3	3	3	3	3	3	3	3	6
Rating scale Odour	3	3	3	3	3	3	3	3	3	6

4.12   Total Coliform and E. Coli

Complete removal of total coliform and E.Coli was achieved when chlorine dioxide was used as a pre-oxidant. Although a reduction in microbiological contaminants is an added advantage when applying a pre-oxidant, it is not the primary objective of the application. However, are shown in **Figure 4.34**, the excellent biocidal properties of chlorine dioxide were demonstrated.

Complete removal of E.Coli and total coliform was obtained at the first process sampling point after pre-oxidation. The highest value recorded for total coliform in the raw water was 19800 cfu/100 mL, with a minimum of 110 cfu/100 mL and an average of 3150 cfu/100 mL being attained. No total coliform was detected in the samples from the downstream sampling points.

The highest value recorded for E.Coli in the raw water was 40 cfu/100 mL, with a minimum of 0 cfu/100 mL and an average of 11 cfu/100 mL being achieved. Similar to the total coliform results, no E. Coli was detected in the samples from the downstream sampling points.
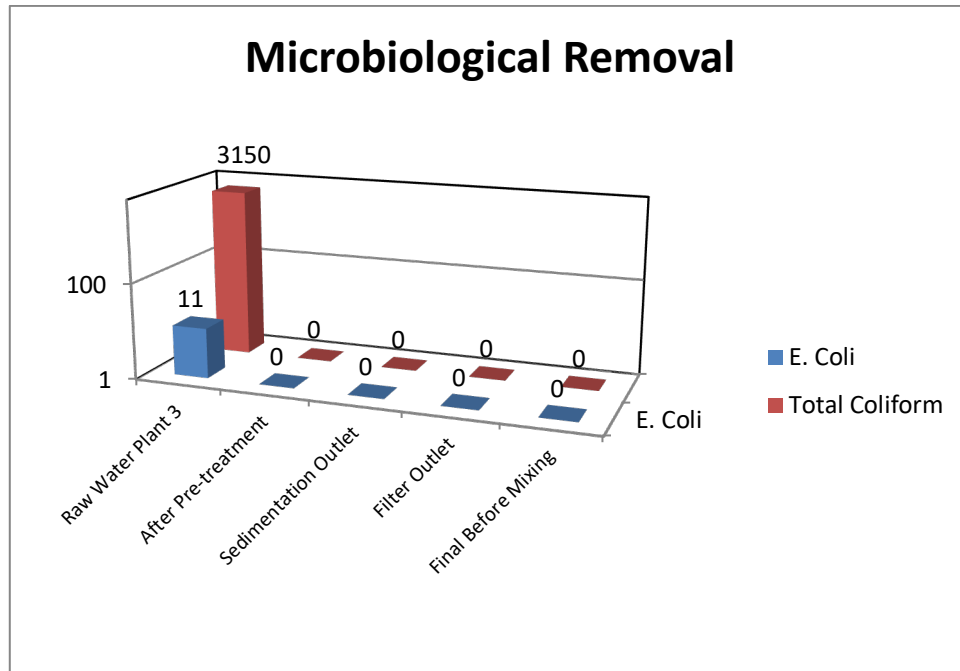
Figure 4.34 Microbiological Removal

4.13   Measurements of Protozoan Parasites and Viruses

Results for the measurements of the presence of cryptosporidium, giardia and enteric viruses are displayed in **Table 4.7**. Due to the high cost of analyses, these measurements were only performed on a quarterly basis during the one-year monitoring period. None of the three viruses were detected during the monitoring period.

Table 4.7. Cryptosporidium, Giardia and Enteric Viruses Measurement

Determinant	Measurement Unit	Raw Water	Final Water
Giardia cysts	Counts / 10L	0	0
Cryptosporidium ocysts	Counts / 10L	0	0
Enteric viruses: PCR	Counts / 10L	0	0

4.14   Cyanobacteria Enumeration and Identification

The algal content in the raw and final water samples is displayed in **Figure 4.35**. The results are plotted on log scale to due to the large difference between the raw and final concentrations.
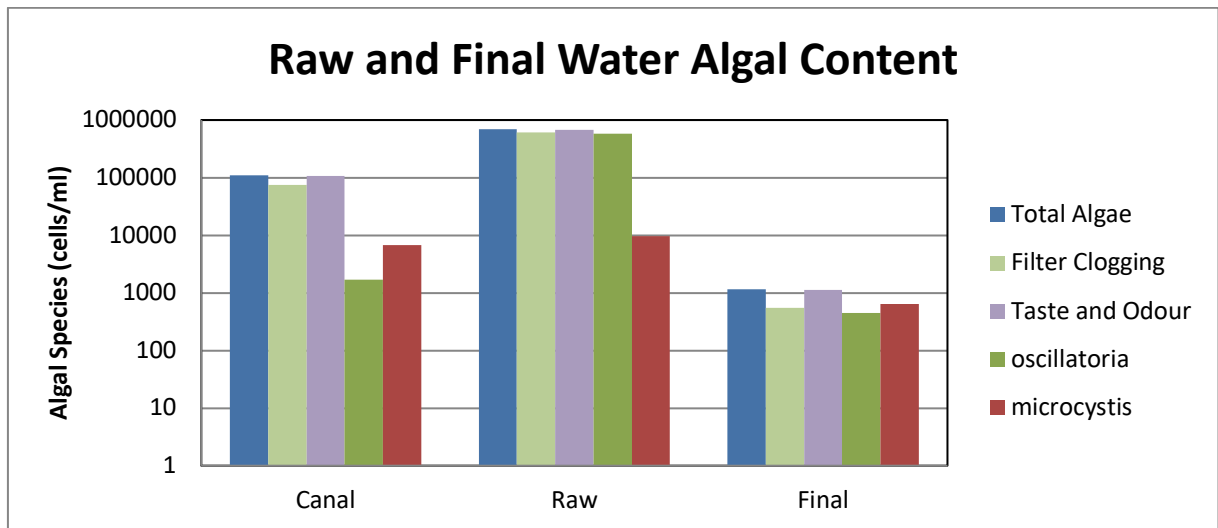

Figure 4.35 Raw and Final Water Algal Content

While microcystis was found to be the dominant species in the canal flowing into the Vaalkop Dam, the oscillatoria species was predominantly present in the dam itself. It should also be noted that out of the total algae concentration, most of the algae present is classified and filter clogging and taste and odour causing species. On average, the oscillatoria and microcystis species was removed to below 1000 cells/mL in the final water.

The total cyanobacteria concentration detected in the raw water is displayed in **Figure 4.36**. The total cell concentration increased during the summer period and the dominant species changed from microcystis (winter months) to oscillatory (summer months). Although an increase in the cell concentration was observed during summer months, the cell concentration during the winter months was also high and exceeded 400 000 cells/ml on three occasions. The highest cell concentration of 1 772 715 cell/mL was recorded in November 2015.
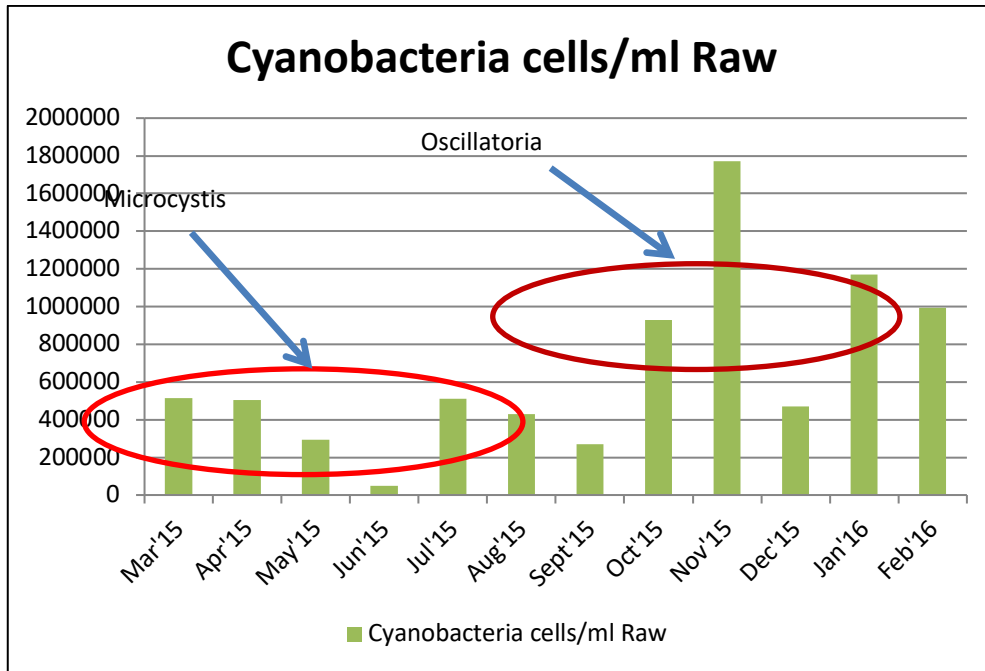
Figure 4.36 Raw and Final Water Algal Content

The removal percentage of cyanobacteria when moving from raw to final water, which is shown in **Figure 4.37**, indicates a near perfect removal of the cyanobacteria. Save for December when chlorine gas was used as a pre-oxidant, chlorine dioxide was used during the entire period. The lowest removal percentage rate of 93%was obtained in December 2015.
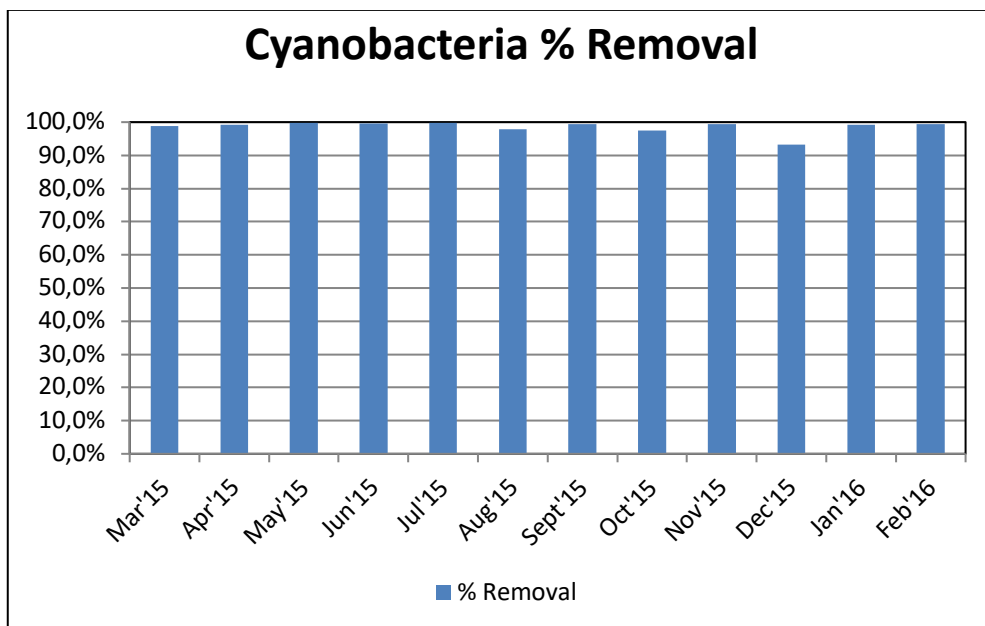

Figure 4.37 Cyanobacteria Removal

4.15   Microcystin Toxins

According to the SANS 241: 2015 Standard, the total microcystin concentration in the final water should be less than 1 µg/l.[11] The measured concentrations of total microcystin toxins in the final water sample are shown in **Figure 4.38**.
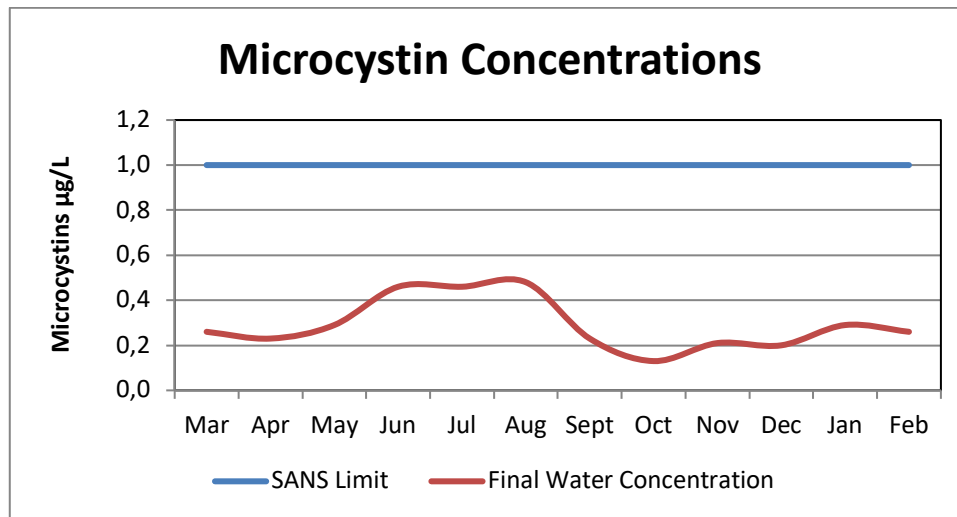
Figure 4.38 Raw Water Microcystin Concentration

It is clear from **Figure 4.38** that the microcystin toxin concentration remained well below the SANS 241 limit during the monitoring period of March 2015 to February 2016. This is despite the presence of very high concentrations of cyanobacteria in the raw water, which has the potential to produce and release toxins into the water.[12]

4.16   Plant Operating Parameters

4.16.1 Treatment Rate

When chlorine gas was use as a pre-oxidant during the algal blooms of the 2013 and 2014 summer months, the filter run timers were as low as 6 hours. During the trial period with chlorine dioxide, very high concentrations of filter clogging algae were also experienced as indicated in **section 4.15**. There were also filter refurbishments taking place in the plant for the entire trial period, and this reduced the available filter capacity from 120ML/d to 105 ML/d.

Despite the high algal concentrations and reduced filtration capacity, the plant was able to run at design capacity and the filter run times increased from 24 to 36 hours. Filter run times when chlorine gas was used as a pre-oxidant was 24 hours. An increase of 25% (12 hours) in filter run times was achieved with the use of chlorine dioxide as a pre-oxidant.

The Vaalkop Water Treatment Plant was extended in 2014. The first phase of the plant extension, which is an additional 30Ml/d treatment capacity, was commissioned in October 2014. The average treatment rate from October 2014 until before the ClO_2 trial period was 195 ML/d.

The average treatment rate during the plant trial was 205 ML/d, which is an increase of 10Ml/d without additional treatment capacity available. It should be noted though that the December treatment rate were lower due to reduced demand during the festive season. The treatment rates are displayed in **Tables 4.8 and 4.9**.

Table 4.8. Treatment Rate Using Cl₂ (before the trial)

Oct 14	Nov 14	Dec 14	Jan 15	Feb 15	Avg
198.3	196.4	191.9	191.1	195.8	194.7

Table 4.9. Treatment Rate Using ClO₂ (during Trial)

Mar15	Apr15	May15	Jun 15	Jul 15	Aug15	Sept15	Oct15	Nov15	Dec15	Avg
200.5	200	203.2	204.3	202.6	209.1	211	205.6	210.5	204.4	205.1

The average plant loss for the trial period was 3.91 %. It should be noted that the last month which is included in the calculation, had a plant loss of 9.9 %. Most of the month the plant was operated without chlorine dioxide and filter run times had to be reduced from 40 to 30 hours after stopping ClO_2. Also, many power failures were experienced and this contributed to plant loss. If the month of December is excluded, the average plant loss for the plant trial period is 3.31 %. During similar algal bloom

periods without ClO_2, plant losses of up to 15 % were recorded. The financial benefit from the increase in production rate can be quantified as follows:

5% increase in production rate amounts to 10 ML/d. At an average cost of R6.50 /kL, the increase in monetary value would be:

10 000 kL/d x 6.50 R/kL = R65 000 per day. This scenario would only apply during times of severe algal blooms when reduced filter run times are experienced.

4.17 Chemical Treatment Cost

The cost of sodium chlorite comprises the largest portion of the ClO_2. The chemical cost of $NaClO_2$ is around R17 per kg, while the cost of chlorine gas is around R13.50 per kg. The generation of 1 kg ClO_2 requires 4.55 kg of $NaClO_2$ and 0.525kg of Cl_2. The chemical cost of 1 kg ClO_2 is thus:

(4.55 x 17) + (0.525 x 13.5) = R84.44 per kg ClO_2. At a dosage of 0.8 ppm which was the average dose during the plant trial and a flow rate of 205 ML/d which was the average plant flow, the treatment cost of chlorine dioxide is as follows:

0.8ppm = 0.8 mg/L = 0.8 kg/ML;
0.8 kg/ML x 84.44 R/kg = 67.55 R/ML = 6.755 c/kL.

At the maximum dosage of 1.5 ppm, the treatment cost increases to:

1.5 kg/ML x 84.44 R/kg = 126.66 R/ML = 12.7 c/kL. The average total treatment cost including the cost of chlorine dioxide amounted to 35.85 c/kL. This figure is significantly higher than of the average cost of 22.3 c/kL without chlorine dioxide for the corresponding period of the previous financial year.

The coagulant demand decreased by 2 mg/l with the use of ClO_2. The coagulant cost during the trial was R8.40 per kg. A reduction in dosage of 2 ppm and a flow rate of 205 ML/d which was the average plant flow, the reduction in treatment cost from the use of chlorine dioxide is as follows:

2 ppm = 2 mg/L = 2 kg/ML;

2 kg/ML x 8.4 R/kg = 16.8 R/ML = 1.68 c/kL.

4.18　Conclusion

The results show that the application of ClO_2 as pre-oxidant at the Vaalkop WTW was beneficial and improved the compliance and quality of the final water. It is a more expensive technology than chlorine gas but is more appropriate to use under certain conditions and is more effective than chlorine especially where the presence of NOM is presenting water quality challenges to the water treatment process.

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CONCLUSIONS AND RECOMMENDATIONS

5.1   Introduction

Chlorine dioxide was tested as an alternative pre-oxidant to chlorine at the Vaalkop Water Treatment Works (WTW). This was necessitated by the deterioration of raw water quality and persistent droughts, which caused high levels of NOM, and coincided with high levels of iron and manganese in the raw water. Apart from water quality problems, reduced filter run times and high treatment plant water losses were experienced.

The aims of the study were:

- To determine the effectiveness of the use of chlorine dioxide as a pre-treatment chemical at the Vaalkop WTW when compared with chlorine gas.
- To determine the economic viability (in terms of cost for potable water treatment) of using chlorine dioxide as a pre-oxidant.
- To determine the conditions under which the different treatment options should be applied to obtain the most effective and efficient result in terms of final water quality and chemical treatment cost.

Chlorine dioxide was generated on site and thereafter directly injected into the raw water pipeline; a contact time of seven minutes before addition of the coagulant at the treatment plant inlet works was used. A full scale plant trial was conducted in parralel with lab scale jar test experiments and over a twelve month period.

The application of chloride dioxide as an alternative pre-oxidant at the Vaalkop WTW was a success based on the results obtained from the assessment of the water quality and treatment plant operational parameters.

5.2   Conclusions

•   The two chemical generation method, which is used for the generation of chloride dioxide by reacting sodium chlorite with chlorine gas, is very efficient and it yielded ≥96% of the desired pre-oxidant.

•   The generation technology used where the precursor chemicals are transported and introduced into the reactor under vacuum and directly injected at the dosing point after generation was found to be effective and safe. The generator operated constantly with little interruption and no safety incidents were reported during the trial period.

•   Chlorine dioxide proved to be more effective than chlorine in the prevention of the formation of DBPs in the final water. Compared to chlorine, which produced bromodichloromethane that was not in compliance with the regulatory limits, no trihalomethane (THM) non-compliances were detected during the trial period when chlorine dioxide was used as a pre-oxidant.

•   Whilst an effective algal removal rate of ≥97% was achieved during cyanobacterial blooms for chlorine dioxide, this dropped to 93% when chlorine was used as a pre-oxidant. The absence of algal toxins in the final water for both Cl_2 and ClO_2 seems to suggest that the algal blooms did not produce any toxins during the trial period.

•   Although no significant difference in the concentrations of geosmin and 2-MIB was detected for the two pre-oxidants (i.e. Cl_2 and ClO_2), the ClO_2 seemed to have brought an improvement in the taste and odour of the final water. This has led the author to conclude that other taste- and odour-forming compounds (other than geosmin and 2-MIB), which were selectively and effectively targeted for removal by ClO_2, were present in the raw water.

•   Despite the presence of high levels of NOM and taste- and odour-causing compounds in the raw water, ClO_2 was able to effectively remove to below the SANS 241 limits the iron and manganese contaminants present in the raw water. The use of Cl_2 under such conditions has, on the other hand, previously led to the formation of trihalomethanes (THMs) and the ineffective removal of the inorganic contaminants (i.e. iron and manganese) as well as taste- and odour-causing agents.

•   Since chlorine dioxide is more expensive than chlorine, an increase of 6.8 c/kl in the chemical treatment at an average dosage of 0.8ppm was noted. The increased chemical treatment costs were, however, offset by the additional benefits associated with the use of ClO_2.

•   A reduction in coagulant demand was able to reduce the treatment cost by 1.68 c/kl, while the 5% increase in the treatment rate during times of severe algal blooms realised an additional financial benefit from the higher volumes of potable water produced. This pre-feasibility assessment seems to indicate that the use of chlorine dioxide is definitely a viable option in potable water treatment during times of poor raw water quality.

•   Chlorine dioxide is definitely a pre-treatment step of choice during periods of high organic loading when reduced filter run times and high plant losses are experienced. It should also be applied during drought periods and/or low dam levels. During such periods, high algal concentrations coincide with anaerobic conditions, which is normally associated with high levels of iron and manganese contaminants in the raw water.

•   The applied ClO_2 dosage was varied from 0.8 ppm to 1.5 ppm for the Vaalkop Dam raw water source. No increased benefits in the removal of contaminants or decrease in coagulant demand was realised at a ClO_2 concentration above 1.5 ppm.

•   The application of chlorine gas as pre-oxidant remains the cheaper of the two options (Cl_2 vs ClO_2) and should be applied during periods of reduced organic loading when high rainfall is experienced and dam levels are high. Chlorine gas is also an efficient and cost effective treatment option to utilise when no taste and

odour problems are experienced and low levels of iron and manganese are present in the raw water.

• Chlorine dioxide should typically be utilised during the South African (SA) summer periods up to the end of dam turnover season. On the other hand, Cl_2 is best utilized during SA winter periods when there is reduced algal growth in the dams. Rainfall patterns also tend to dictate the treatment regime that needs to be adopted; depending on the quality of the raw water, ClO_2 and Cl_2 should, respectively, be used during drought and high rainfall periods.

5.3   Recommendations

The following pertinent issues were not tackled under this research study and would require to be addressed in future studies:

- The formation of chlorates in the final water was not measured due to a number of constraints. Although it is not a regulated parameter in South Africa, it remains an important factor to consider and is regulated in the United States, Europe and by the World Health Organisation (WHO). The degree of formation of chlorates at different dosages of ClO_2 should be monitored and the maximum dosage of ClO_2 that can be applied and still comply with the WHO standard should be determined.

- It remains unclear when the formation of DBPs can be expected and therefore when a switch should be made from Cl_2 to ClO_2. A prediction of the potential for the formation of DBPs can only be carried out by fractionation of NOM and determining which specific fraction of NOM is responsible for the formation of the DBPs in the raw water of the Vaalkop Dam.

Due to the high return flows received in the catchment of the Vaalkop Dam, the presence of emerging contaminants and endocrine disrupting compounds (EDCs) are of concern and the effect of ClO_2 on these substances should be investigated.