Department of Chemistry

Advanced Water Treatment Technologies to Minimise the Formation of Emerging Disinfection By-Products in Potable Water

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DECLARATION

To the best of my knowledge and belief, this Thesis contains no material previously published by any other person except where due acknowledgement has been made.

This Thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:

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Date:

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LIST OF ABBREVIATIONS

AOC	assimilable organic carbon
BAC	biological activated carbon
BCAA	bromochloroacetic acid
BCAN	bromochloroacetonitrile
BDCAA	bromodichloroacetic acid
BDCAN	bromodichloroacetonitrile
BDOC	biodegradable dissolved organic carbon
Br-/Cl-THMs	mixed bromo-/chloro-trihalomethanes
Br-DBPs	brominated disinfection by-products
BRP	bacterial regrowth potential
CDBAA	chlorodibromoacetic acid
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CWQRC	Curtin Water Quality Research Centre
DBAA	dibromoacetic acid
DBAN	dibromoacetonitrile
DBCAN	dibromochloroacetonitrile
DBP	disinfection by-product
DCAA	dichloroacetic acid
DCAN	dichloroacetonitrile
DCM	dichloromethane
DOC	dissolved organic carbon
DPD	*N*,*N*-diethyl-*p*-phenylenediamine
DR	diluted raw water
EI	electron impact
EU	European Union
FA	fulvic acid
GAC	granular activated carbon
GC-MS	gas chromatography-mass spectrometry
GWTP	groundwater treatment plant
HA	humic acid

HAA	haloacetic acid
HAAFP	haloacetic acid formation potential
HAA9	combination of nine haloacetic acids
HANs	haloacetonitriles
HAN5	combination of five haloacetonitriles
HOBr	hypobromous acid
HOCl	hypochlorous acid
HOI	hypoiodous acid
HPLC	high performance liquid chromatography
IC	ion chromatography
I-DBPs	iodinated disinfection by-products
I-THMs	iodinated trihalomethanes
IWSS	integrated water supply system
LOD	limit of detection
MAC	Maximum acceptable concentration
MBAA	monobromoacetic acid
MBAN	monobromoacetonitrile
MCAA	monochloroacetic acid
MCAN	monochloroacetonitrile
MIEX®	magnetic ion exchange
mins	minutes
MtBE	methyl *tert*-butyl ether
MW	molecular weight
NDBA	*N*-nitrosodi-n-butylamine
NDBA-d9	*N*-nitroso-(n-butyl-d9)-amine
NDEA	*N*-nitrosodiethylamine
NDEA-d10	*N*-nitrosodiethyl-d10-amine
NDMA	*N*-nitrosodimethylamine
NDMA-d6	*N*-nitrosodimethyl-d6-amine
NDPA	*N*-nitrosodi-n-propylamine
NDPA-d14	*N*-nitrosodi-n-propyl-d14-amine
NDPhA	*N*-nitrosodiphenylamine
NEMA	*N*-nitrosoethylmethylamine

NF	nanofiltration
NMOR	*N*-nitrosomorpholine
NMOR-d8	*N*-nitrosomorpholine-d8
NOM	natural organic matter
NPIP	*N*-nitrosopiperidine
NPIP-d10	*N*-nitrosopiperidine-d10
NPYR	*N*-nitrosopyrrolidine
NPYR-d8	*N*-nitroso-pyrrolidine-d8
PAC	powdered activated carbon
PC	post-clarified water
pCBA	*para*-chlorobenzoic acid
PF	post-filtration water
RO	reverse osmosis
SUVA	specific ultraviolet absorbance
$SUVA_{254}$	specific ultraviolet absorbance at 254 nm
SPE	solid phase extraction
SPME	solid phase micro-extraction
TBAA	tribromoacetic acid
TBAN	tribromoacetonitrile
TCAA	trichloroacetic acid
TCAN	trichloroacetonitrile
TDS	total dissolved solids
THMs	trihalomethanes
THMFP	trihalomethane formation potential
THM4	sum of four regulated trihalomethanes
TOC	total organic carbon
UF	ultrafiltration
UK	United Kingdom
US-EPA	United States Environmental Protection Agency
UV	ultraviolet
VUV	vacuum-ultraviolet
WA	Western Australia
WCWA	Water Corporation of Western Australia

WHO	World Health Organization
X_2AAs	dihalogenated acetic acids
X_3AAs	trihalogenated acetic acids

The term ‘chloramine’ refers to the use of monochloramine.

ABSTRACT

As the international standards for drinking water become more stringent and the health guideline values for currently regulated disinfection by-products (DBPs) decrease, the challenge increases for water utilities to produce water which conforms to the guidelines. In Australia, expanding populations, and drought in some areas, particularly Western Australia, have already resulted in scarcity of water in many urban and regional centres. As a result, water of more marginal quality must be utilised for potable purposes, and the variable and more concentrated natural organic matter (NOM) in these water sources makes the treatment, distribution, and disinfection processes increasingly difficult.

While NOM itself does not appear to be harmful, when it reacts with disinfectants, some of the resulting DBPs have been found to be potentially harmful to human health. Due to concerns about these potential health effects, other disinfection methods aimed at reducing the major DBPs from chlorination, such as the trihalomethanes (THMs), have been investigated. Chloramination is increasingly being used as an alternative disinfection method to chlorination, because it has the advantage of producing only trace amounts of THMs and haloacetic acids (HAAs). However, chloramination can result in the formation of other DBPs, some of them newly identified and termed 'emerging DBPs', such as the *N*-nitrosamines, with many of the emerging DBPs being reported to be carcinogenic, mutagenic, and/or teratogenic. For the purpose of this Thesis, 'emerging DBPs' refers to DBPs which have little or no regulations or guideline values assigned to them.

An effective approach to reducing the formation of potentially harmful DBPs is to remove the DBP precursors prior to the disinfection stage. For removal of dissolved organic carbon (DOC) as a DBP precursor, it is becoming increasingly common for ozone to be used as a pre-oxidant or intermediate oxidant during drinking water treatment. Ozone followed by biological activated carbon (BAC) filtration has been shown to improve water quality by removing a portion of the DOC, depending on the content of ozone-reactive DOC within the water source. However, in bromide-

containing waters, ozonation can result in the formation of bromate, a potent carcinogen. Advanced oxidation processes (AOPs), which usually involve the addition of a combination of chemical oxidants and/or a source of UV light, are also attracting increasing interest as DOC removal techniques.

This Thesis focuses primarily on the formation of DBPs under conditions that are particularly relevant to Western Australian water quality issues, since the project formed part of the Australian Research Council (ARC) Linkage project LP0882550, with Western Australian industry partner organisations, Water Corporation and GHD Pty Ltd. The following sub-topics were studied: reactions of DBP precursors (NOM, bromide, and iodide ions); impact of type of disinfectant used (chlorine and monochloramine (the latter will be referred to as 'chloramine' in this Thesis)); reactions of ozone as an oxidant; and effect of pH on DBP formation. Laboratory-scale experiments were performed to study DBP formation reactions under a variety of conditions.

The formation of specific DBPs was studied, with specific compounds including: the THMs (the regulated brominated and chlorinated THMs (THM4: chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and the six iodinated THMs (I-THMs: bromochloroiodomethane, dibromoiodomethane, bromodiiodomethane, dichloroiodomethane, chlorodiiodomethane, and iodoform)); the nine HAAs (HAA9: monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, chlorodibromoacetic acid, trichloroacetic acid, and tribromoacetic acid); five haloacetonitriles (HAN5: chloroacetonitrile, bromoacetonitrile, dichloroacetonitrile, dibromoacetonitrile, bromochloroacetonitrile, trichloroacetonitrile, tribromoacetonitrile, dibromochloroacetonitrile, and bromodichloroacetonitrile); eight *N*-nitrosamines (*N*-nitrosodimethylamine, *N*-nitrosoethylmethylamine, *N*-nitrosodiethylamine, *N*-nitrosodi-n-propylamine, *N*-nitrosodi-n-butylamine, *N*-nitrosodipiperidine, *N*-nitrosopyrrolidine, and *N*-nitrosomorpholine); and bromate and iodate.

In Chapter 2, several oxidation and AOP techniques which have potential for DOC removal prior to disinfection and distribution of drinking water are reviewed. The

oxidation and AOP methods discussed are ozone, peroxide, UV, ferrate^{VI}, and (photo-) Fenton's reagent, and combinations of these. The design and construction of a water treatment rig with facilities for all of these processes, which evolved through consultation and collaboration with researchers from the Curtin Water Quality Research Centre (CWQRC), engineering consultants and partner organisation GHD Pty Ltd, the local water utility (Water Corporation of Western Australia), and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Scientific Engineering Unit, Waterford, is also described. The rig will allow water samples to be treated using various oxidation and AOP methods, coupled with biological or abiotic activated carbon, enabling detailed studies on the effectiveness of these treatments in their removal of DBP precursors.

In Chapter 3, the formation of eight *N*-nitrosamines and three classes of halogenated DBPs (THM4, HAA9, and HAN5) from chlorination and chloramination of a surface water drinking water source, containing relatively high concentrations of DOC and bromide, was studied. Chloramine was found to generate significantly lower concentrations of THM4, HAA9, and HAN5 than chlorine. Bromine incorporation into the DBPs was found to be significantly higher with the use of chlorine compared to chloramine. Low concentrations of *N*-nitrosodimethylamine (NDMA) and *N*-nitrosodiethylamine (NDEA) were detected as a result of chlorination and chloramination treatment of the source water, where the disinfectant concentrations were 7 and 3 mg L^{-1}, respectively. This is the first report of the formation of *N*-nitrosamines other than NDMA, as well as the formation of *N*-nitrosamines from chlorination, in Australian drinking water systems. However, a study of the total *N*-nitrosamine formation potential (10 days, large excess of chlor(am)ine) showed that, with the higher chloramine concentration, the formation of these two *N*-nitrosamines increased significantly, while their concentrations did not increase with the higher chlorine concentration. This is the first reported total formation potential values for the seven analysed *N*-nitrosamines other than NDMA, with a detectable value for NDEA observed.

The effect of chlorination and ozonation on THM, bromate, and iodate formation in a groundwater containing high bromide concentrations is presented in Chapters 4, 5, and 6. In Chapter 4, an investigation into the positioning of a potential ozonation step

at the Jandakot Groundwater Treatment Plant (GWTP) is described. Batch experiments were performed on three water samples taken through the treatment process: raw water, a water sample post-clarification, and a water sample post-filtration. It was determined that an ozonation step should be located between the clarification process and filtration, as this would be a more economical option due to NOM removal during coagulation, thereby reducing the required ozone dose. A biological filtration step following ozonation would then remove biodegradable organic ozonation products, resulting in improved water quality and a decrease in DBP formation upon chlorination for final disinfection.

In Chapters 5 and 6, investigations of the effects of pH, pre-chlorination, and initial ozone concentration on THM (THM4 and I-THMs) and bromate formation in Jandakot GWTP post-clarified water are described. Kinetic ozonation experiments showed that the ozone chemistry did not significantly alter between samples taken on different production days when the GWTP processed different volumes from a variety of bores. In addition, ozone was found to be more stable at pH 6.5 than 7.5, which is potentially advantageous as the average pH at the GWTP during this study was 6.4. Ozonation experiments showed that bromate and bromoform formation increased with increasing initial ozone concentration, while concentrations of the remaining three regulated THMs remained constant, at both pH 6.5 and 7.5. Pre-chlorination of the samples prior to ozonation resulted in an increase in bromoform and the mixed Br-/Cl-THMs, and an investigation using the model compound resorcinol showed the increase was likely a result of the organic THM precursors, which were partially halogenated during the pre-chlorination step, then reacting with HOBr to form THMs during ozonation. Three I-THMs were detected in the post-clarified water sample collected from the plant: $CHClI_2$, CHBrClI, and $CHBr_2I$. The concentrations of these I-THMs were found to increase according to $CHBr_2I$ < CHBrClI < $CHCl_2I$, and there did not appear to be a significant difference between I-THM or iodate formation at pH 6.5 and 7.5. At pH 6.5, all three I-THMs were found to decrease with increasing initial ozone concentration. However, at pH 7.5, the $CHBr_2I$ was observed to increase with initial ozone concentration. Chlorination of the post-clarified sample had a significant effect on I-THM and iodate formation. The relatively high concentration of ammonia present in the sample presumably formed chloramine upon chlorination. Chloramine does not oxidise HOI to iodate,

thereby allowing HOI to react with NOM and form I-THMs. Chlorine doses ≤ 2 mg L^{-1} (i.e. ≤ equivalent ammonia concentration) resulted in increasing I-THM formation and similar iodate formation with increasing initial chlorine concentration, consistent with chloramine being the major oxidant. A higher initial chlorine concentration resulted in significantly lower I-THM formation and higher iodate formation, indicating the presence of free chlorine equivalents, thereby promoting the oxidation of HOI to iodate. Ozone treatment of the post-clarified water sample was found to significantly increase iodate formation, as well as degrade two of the three detected I-THMs ($CHCl_2I$ and CHBrClI). The third I-THM, $CHBrI_2$, was found to increase slightly after ozonation, possibly due to reaction between residual HOBr and iodo-organic THM precursors after complete ozone depletion.

In this research, the formation of DBPs, including emerging DBPs that had not previously been studied in Western Australian drinking waters, was investigated. High THM4 formation in the surface drinking water source, as well as the detection of NDMA and NDEA, the latter not previously reported in Australian drinking water systems, emphasised the importance of regular DBP monitoring within distribution systems. The position and optimisation of an ozonation step within a water treatment process was demonstrated to be essential to the production of drinking water with DBP concentrations within regulation values. Ozonation after a NOM reduction process, such as clarification, ensures the economical application of ozone; whilst subsequent biofiltration following ozonation will reduce the concentrations of biodegradable organic ozonation products, thus resulting in decreased DBP formation upon final disinfection. In addition, the clarification process at the Jandakot GWTP stabilised the water blends, rendering them to be of similar quality, thereby confirming an ozonation step would be most efficient after the clarification step. Optimisation of the ozone process was found to be essential for an appropriate balance between bromoform and bromate formation in order to comply with their respective guideline values, since for ozonation of bromide-containing waters, a decrease in bromate formation results in an increase in bromoform production. Chlorination (at concentrations resulting in free chlorine equivalents) and ozonation may be possible solutions for controlling the formation of I-THMs, and their accompanying taste and odour issues, as well as the formation of other potentially toxic organic I-DBPs, in iodide-containing waters. Lowering the pH may also be

beneficial in ozone water treatment processes, as bromate formation decreases, while iodate formation remains unaffected. In conclusion, this project has furthered the understanding of the formation of emerging DBPs, e.g. the *N*-nitrosamines, I-THMs, bromate, and iodate, for the Western Australian water industry, as well as the broader research community.

PRESENTATIONS ARISING FROM THIS THESIS

Caroline E. Nottle (née Taylor)

Oral Presentations

Caroline E. Nottle, Urs von Gunten, Cynthia Joll, and Anna Heitz (2011) THM and Bromate Formation of Waters Containing High Bromide Concentrations during Multistep Treatment with Chlorine and Ozone, CWQRC Disinfection By-Product Workshop, Curtin University, 17th May 2011

Caroline E. Taylor, Urs von Gunten, and Scott Garbin (2009 and 2010) Jandakot Ozonation Trials Update, Project Updates to Water Corporation, October 2009 and February 2010

Conference Poster Presentations

Caroline E. Taylor, Daniel Visser, Cynthia Joll, Anna Heitz, and Urs von Gunten (2010) A Flexible Rig with Multiple Oxidation Processes for the Transformation of Natural Organic Matter to Minimise Disinfection By-Product Formation, Ozwater'10, Brisbane, 6th – 10th March 2010

Caroline E. Taylor, Cynthia Joll, and Anna Heitz (2009) Disinfection By-Product Formation from Chlorination and Chloramination of a Western Australian Surface Water, Gordon Research Conference on Drinking Water Disinfection By-Products, Massachusetts, 9th – 14th August 2009

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REFEREED ARTICLES ARISING FROM THIS THESIS

Caroline E. Nottle (née Taylor)

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Refereed Conference Articles

Joll, C., Allard, S., Nottle, C., Heitz, A. and von Gunten, U. (2013) *Mitigation of the formation of iodo-organic disinfection by-products through ozonation pre-treatment.* Ozwater'13, Perth, 7-9 May, 2013

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LITERATURE REVIEW

1.1 Introduction

The treatment and disinfection of water for drinking purposes is critical to the protection of human health through elimination of pathogens and prevention of the spread of waterborne diseases. The drawback to disinfection is the formation of disinfection by-products (DBPs) which result from reactions of the oxidant (i.e. disinfectant, of which chlorine is the most commonly used) with the organic and inorganic matter present in all raw waters. In 1974, it was discovered that chlorination of surface waters produced trihalomethanes (THMs) (Bellar et al. 1974; Rook 1974), and one of these by-products (chloroform) was subsequently linked to cancer in laboratory animals (NCI 1976). Since then, over 700 DBPs have been identified (Krasner et al. 2006; Richardson 2011), and several toxicological and epidemiological studies have been conducted to measure and evaluate the health risks of DBPs in drinking water (Richardson 2003; Richardson et al. 2007). In response to these discoveries, many countries have applied regulatory standards or maximum guideline values for some of these DBPs.

In order to balance microbial inactivation with DBP control, an understanding of the rate and extent of DBP formation during disinfection is required. There have been several approaches to control the formation of DBPs, such as the removal of precursor material prior to disinfection, the adjustment of disinfectant dosing location, and the alteration of disinfectant dose and type (Singer 1999). Reducing the applied disinfectant dose has its limitations, as a sufficient disinfectant residual is required within the distribution system to ensure pathogen control. Several alternative disinfection treatment methods aimed at reducing the major DBPs have been investigated over the years. Ozone (Richardson et al. 1999a) and chloramine (Seidel et al. 2005) have attracted increasing interest as alternative disinfectants to chlorine. However, all chemical disinfection methods produce a range of DBPs in various concentrations, with substantial variations in their toxic properties (Krasner et al. 2006). In addition to DBP formation, the reaction of disinfectants with natural organic matter (NOM) also results in the formation of bioavailable organic matter, which stimulates microbial regrowth. Microbial regrowth leads to the formation of biofilms within the distribution system, which can harbour pathogenic microorganisms, form taste and odour compounds, and consume disinfectant (Franzmann et al. 2001). It is therefore important to remove organic matter, the

major precursor to DBPs, prior to disinfection in order to avoid deterioration of the distributed water (off-flavours and disinfection by-product formation) and distribution system (microbial regrowth) quality (Camel and Bermond 1998).

There are several technologies available for the removal of NOM prior to final disinfection. Conventional drinking water treatment removes NOM via coagulation and filtration, however due to DBP regulations becoming increasingly stringent, new treatment technologies are continually being explored. Methods such as membrane filtration, activated carbon adsorption, magnetic ion exchange resin (MIEX®), ozonation, and advanced oxidation processes (AOPs) have all been investigated and applied as advanced DBP precursor removal technologies in drinking water treatment plants.

1.2 Natural Organic Matter (NOM)

Natural organic matter (NOM) is a complex heterogeneous mixture of compounds derived from plants, animals, and microorganisms; and varies depending on the source from which it is derived, as well as the climatic and environmental conditions to which it has been exposed. Depending on its origin and age, NOM varies in molecular size, chemical composition, structure, and polyelectrolytic characteristics (Chin et al. 1994; Chin et al. 1998; Chen et al. 2002). In natural waters, the NOM content varies between geographical sources, and may have seasonal (e.g. flushing of organic matter from soils at the beginning of the rain season) and spatio-temporal variation within the same source (Biber et al. 1996; Sharp et al. 2006a; Fabris et al. 2008).

NOM is difficult to define, both chemically and physically, as it incorporates compounds which can only be broadly characterised. It consists of hydrophobic and hydrophilic substances and, in general, the hydrophobic substances make up approximately 50% of the total organic carbon (TOC) (Thurman 1985). Hydrophobic NOM is rich in aromatic carbon, phenolic structures, and conjugated double bonds, while hydrophilic NOM contains more aliphatic carbon and nitrogenous moieties, such as carbohydrates, proteins, and amino acids (Korshin et al. 1996; Swietlik et al. 2004).

According to long established soil science terminology, the hydrophobic substances can be further partitioned into three groups based on their solubility properties in aqueous solutions: humic acids (HA), fulvic acids (FA), and humin (Thurman 1985; Schwarzenbach et al. 1993). Humic acids are not soluble in water under acidic conditions (pH < 2), but become soluble at higher pH, and are often referred to as being the high molecular weight fraction, with weights ranging from 1500 to 5000 Da in streams (Malcolm 1990). Fulvic acids are referred to as moderate molecular weight substances ranging from 600 to 1000 Da in streams, and are soluble under all pH conditions (Malcolm 1990). Humin is defined as the fraction that is not soluble in water at any pH value. In comparison to the stream water described by Malcolm (1990), the molecular weight of fulvic and humic acids in Australian freshwaters, which are usually reservoirs, lakes, and rivers, can range from below 500 to > 10 000 Da (Newcombe et al. 1997).

In natural waters, organic matter ranges from free monomers to macromolecules and colloids to aggregates and large particles (Thurman 1985). These can be classified into two groups by operational definition: particulate organic matter is the organic matter retained on a 0.45 µm membrane upon filtration, and the organic matter which passes through the membrane in the filtrate is called dissolved organic matter (Spitzy and Leenheer 1991). The concentration of dissolved organic matter is typically determined as dissolved organic carbon (DOC), which is measured via conversion of the organic carbon to carbon dioxide, using methods based on high-temperature catalytic oxidation, ultraviolet/persulphate oxidation, or a combination of these processes, and the carbon dioxide concentration is then measured and converted to a concentration of DOC. Aromatic units in the NOM structure absorb light, especially at wavelengths greater than 250 nm (Korshin et al. 1996). The absorbance at 254 nm (UV_{254}) is often measured on water samples containing NOM and then used as an approximate indicator of the overall aromatic content of the NOM. The specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) is the ratio of UV absorbance (cm^{-1}) to DOC concentration (mg L^{-1}) multiplied by 100, and has been used as a surrogate for the humic content of a water (Hwang et al. 2000; Boyer and Singer 2006). The $SUVA_{254}$ is indicative of the relative aromatic carbon content in NOM, and, generally, high SUVA waters tend to contain more hydrophobic NOM and have low

ionic strength, while low SUVA waters tend to contain a higher content of hydrophilic NOM (Boyer and Singer 2006).

There is no evidence that NOM itself is harmful, however it can have a significant impact on drinking water quality. NOM can adversely impact water treatment processes by fouling of membranes and consumption of disinfectants and other water treatment chemicals. NOM promotes the formation of biofilms which, in themselves, lead to fouling of infrastructure and production of substances that consume disinfectants (e.g. sulphides, nitrite, and organic metabolites). Bacteria are able to proliferate within distribution systems if dissolved organic matter and other nutrients (e.g. ammonia and phosphorous) are not sufficiently removed (Simpson 2008). This bacterial re-growth can result in the formation of off-flavour compounds, accelerate corrosion within the distribution system, and promote the risk of pathogen growth (Okabe et al. 2002).

In finished waters, NOM can produce an undesirable colour, as well as react with disinfectants to form disinfection by-products (DBPs), some of which may be potentially harmful to human health. The removal of NOM prior to disinfection can minimise the formation of DBPs, and the many other water quality problems that are caused directly or indirectly by this matter.

1.3 Treatment Processes for NOM and DBP Precursor Removal

Removal of the DBP precursors, bromide and NOM, has been the focus of many advances in water treatment technologies, including (individually or in combination) coagulation/enhanced coagulation, biofiltration, membrane processes, MIEX®, ozone, and, to a lesser extent, advanced oxidation processes (AOPs). Processes such as adsorption or coagulation remove the precursors intact, while processes such as oxidation transform the precursors into oxidation by-products which may be more or less reactive with the applied disinfectant (Amy et al. 1991).

1.3.1 Coagulation

Coagulation is an important process for drinking water treatment as it creates aggregates of small particles onto which DOC can be adsorbed, and can then be removed by sedimentation and filtration. Conventional coagulation is usually

optimised to remove turbidity, while enhanced coagulation is typically optimised for maximum NOM removal. Enhanced coagulation differs from coagulation in that higher coagulant doses, and reduced pH are used (White et al. 1997). The coagulant (iron or aluminium salts) rapidly hydrolyses to form insoluble, positively charged precipitates in water (Bond et al. 2011). NOM is then removed via the mechanism of charge neutralisation for colloidal material, and charge complexation/precipitation for soluble compounds, with additional removal occurring due to adsorption onto the precipitated flocs and metal hydroxides (Randtke 1988).

The treatment preferentially removes anionic DBP precursors, which are typically hydrophobic and high molecular weight (White et al. 1997; Liang and Singer 2003; Sharp et al. 2006b). Once the coagulant demand for the hydrophobic organic material is satisfied, a greater amount of hydrophilic organic material can be removed (White et al. 1997). The efficiency of coagulation and flocculation is dependent on the nature of the NOM present in the source water, both the concentration and the composition and character (Sharp et al. 2006a).

Bromide is generally not removed during coagulation, therefore the ratio of bromide to DOC increases after coagulation treatment, resulting in a shift in the DBP speciation towards a higher level of bromination within DBPs (Boyer and Singer 2005).

1.3.2 Treatment Methods Based on Activated Carbon

Activated carbon (AC) is used in water treatment for the removal of NOM, specific contaminants (e.g. pesticides), and taste and odour compounds, and is used as either powdered activated carbon (PAC) or granular activated carbon (GAC). PAC can be applied at various stages throughout water treatment, and doses are typically between 5 and 25 mg L^{-1} (Bond et al. 2011). GAC is usually used after coagulation/sedimentation, prior to final disinfection. AC has unique adsorption properties, which are a result of the high surface area, micropores, and broad range of surface functional groups (Karanfil and Kilduff 1999).

The mechanism for the sorption of NOM to the AC is the reversible physical adsorption caused by non-specific forces (e.g. van der Waals forces, dipole

interactions, and hydrophobic interactions), in which small, neutral, hydrophobic molecules are adsorbed (Weber Jr et al. 1991). Hydrophilic substances have a low adsorption affinity for AC, as they are more soluble in water (Karanfil and Kilduff 1999). Size exclusion has also been reported as a mechanism for NOM removal on AC, with smaller humic acid molecules being preferentially adsorbed (Kilduff et al. 1996). Organic molecules of smaller molecular size have higher diffusion coefficients, and are able to reach the adsorbent surface more quickly than larger molecules, where they are then able to diffuse into the adsorbent pore structure and access a greater adsorbent surface area (Kilduff et al. 1996). The average dissolved organic matter size has been reported to be in the 4 – 40 Å range, and it has been found that, in regard to NOM uptake, AC with a larger pore size performs more effectively (Karanfil and Kilduff 1999).

There are limitations associated with the use of AC filters. When all the available adsorption sites become fully saturated with organic matter, breakthrough occurs and organic matter increasingly passes through the filter, leading to a deterioration in water quality. Backwashing is not able to remove organic matter adsorbed to the AC particles, and as a result, the AC media must be replaced or thermally regenerated when it becomes exhausted in order to restore its efficiency (Ghosh et al. 1999).

1.3.3 Biofiltration

Biofiltration, or biotreatment, utilises the development of a biofilm on a sand or AC medium to remove micro-organisms and organic and/or inorganic matter. The active biofilm on biological activated carbon (BAC) filters can process and biodegrade significant fractions of entrapped waterborne nutrients within the GAC pores, dissolved organic matter adsorbed to the GAC surfaces, as well as other contaminants, minerals, and microorganisms (Simpson 2008). BAC filters are advantageous compared to GAC filters in that the bed lifetime can be extended, and the long term organic matter removal efficiencies are higher (Scholz and Martin 1997).

The main methods of NOM removal during biofiltration are adsorption and enzyme-controlled microbial degradation (Bond et al. 2011). Substrate mass transport and biodegradation kinetics control the rate of biodegradation (Huck et al. 1994). Small

compounds are generally more biodegradable than larger compounds. BAC treatment will only have an impact on NOM and DBP precursor removal if and where the reactive precursors are readily biodegradable (i.e. waters containing high amounts of biologically derived NOM): therefore in order to increase the effectiveness of biofiltration, oxidative pre-treatments, such as ozonation or AOPs, have been used to enhance the biodegradability of NOM (Bond et al. 2011).

Several researchers have reported reductions in DOC concentration and/or DBP formation after biofiltration, as well as after oxidation followed by biofiltration. For example, Toor and Mohseni (2007) observed average reductions of 11% and 42% for concentrations of THMs formed after chlorination of water samples collected after biofiltration and UV-H_2O_2-biofiltration, respectively, compared to chlorination of untreated raw surface water.

1.3.4 Membrane Processes

Within the water industry, there is interest in the use of membranes for the removal of DBP precursors, particles (turbidity), and microorganisms, with the use of a post-membrane filtration disinfectant (Siddiqui et al. 2000). Four types of membrane processes are common in water treatment: microfiltration, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). When using membranes that have a surface charge, the rejection of molecules occurs through size exclusion and electrostatic repulsion, while for tighter membranes, there is the additional rejection process of the differing diffusion rates of various solutes across the membrane (Bond et al. (2011) and references therein). Therefore, types of molecules removed depend on the properties of the membrane surface. When molecular size is below the molecular weight cut-off of the membrane, hydrophobicity is the most important parameter, with hydrophobic compounds permeating relatively easily though a membrane, while hydrophilic compounds are more likely to be rejected (Braeken et al. 2005).

NF or RO membranes are required for DBP precursor removal due to the small size of the DBP precursors (e.g. Chellam 2000; Siddiqui et al. 2000), and are advantageous as both methods have the capability to simultaneously remove organic (NOM) and inorganic (halides, such as bromide and iodide) precursors (Watson et al.

2012). The main issue with the use of membranes is the requirement for pre-treatment to minimise colloidal/mineral fouling (Siddiqui et al. 2000), which results in permeate flux deterioration (Song et al. 2004). For example, minimal pre-treatment for an NF filter would consist of: scale control (via addition of an acid and/or an anti-scalant), and pre-filtration using cartridge filtration or MF/UF for particle/colloid removal (Siddiqui et al. 2000).

1.3.5 The MIEX® Resin Process

The MIEX® process is a recently developed method specifically designed for the removal of NOM (Warton et al. 2007). The process can be used as an alternative to coagulation, or as a pre-treatment to coagulation to reduce coagulant doses (Bond et al. 2011). Its use as a pre-treatment prior to coagulation has been shown to significantly reduce DBP formation (between 50 – 70 % reduction in THMs, and > 60 % reduction in HAAs) when compared to conventional coagulation treatment (Singer and Bilyk 2002; Fearing et al. 2004; Mergen et al. 2008).

The MIEX® resin is a strong base anion exchange resin with quaternary ammonium functional groups and consists of 150 – 180 µm particles on a macroporous, polyacrylic structure (Singer and Bilyk 2002). Anion exchange is carried out on the quaternary ammonium sites, where organic and inorganic anions are exchanged with chloride ions (Warton et al. 2007). The high density and magnetic properties of the resin results in rapid exchange and settling and, after settling, between 90 and 95 % of the resin is usually recycled back into the contactor, with the remainder regenerated with a 10 % sodium chloride solution at pH 10 (Warton et al. 2007).

The extent of NOM removal using the MIEX® method is dependent on the characteristics of the raw water. For example, Mergen et al. (2008) performed batch MIEX® experiments on three raw waters with fundamentally different NOM character (reservoir, river, and surface water), though the waters had similar DOC content (9.4 – 10.7 mg L^{-1}). It was found that both hydrophilic and hydrophobic NOM can be removed by the resin, and that high molecular weight (MW) NOM quickly saturated or blocked the resin. Consistently high removal was achieved for water dominated by hydrophilic acids, while algogenic-derived NOM was poorly removed (Mergen et al. 2008). The MIEX® process has an additional benefit of

potentially being able to remove bromide, thus reducing the formation of brominated DBPs upon disinfection of the product water. However, the extent of bromide removal is reported to decrease with increasing alkalinity and bromide concentrations (Johnson and Singer 2003), and other investigators have found bromide was not substantially removed at all (Warton et al. 2007). Warton et al. (2007) observed minimal bromide removal during large-scale MIEX® application at a groundwater treatment plant (DOC: 6.85 and 4.15 mg L^{-1}, bromide: 0.5 and 0.58 mg L^{-1} for summer and winter samples, respectively), and it was surmised that bromide would only be removed by adjusting plant operating parameters to allow the increase of fresh resin into the system, rather than using only regenerated resin, to compensate for competition between anions for active sites on the resin.

1.3.6 Ozone

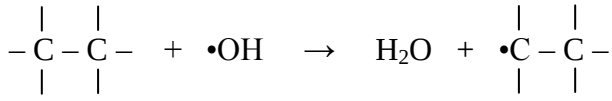
Ozonation is an established method for water treatment, and is typically utilised for disinfection, removal of colour, and improvement of taste and odour characteristics, as well as the oxidation of specific organic and inorganic micro-pollutants (von Gunten 2003b), rather than bulk NOM removal. Lower ozone doses ($\leq$ 0.5 mg O_3/mg DOC) are generally applied for microflocculation enhancement, while higher doses ($\geq$ 1.0 mg O_3/mg DOC) are used for the oxidative destruction of NOM (Amy et al. 1991).

Oxidation of NOM during ozonation can occur through reactions with both ozone and hydroxyl radicals (•OH), the latter of which are formed via the decomposition of ozone (Hoigne and Bader 1976). However, when compared to AOPs, ozone produces smaller concentrations of •OH. Ozone reacts with NOM as an electrophile, preferentially oxidising the electron-rich moieties such as olefinic structures and aromatic alcohols (Hoigne and Bader 1983a; Hoigne and Bader 1983b), eventually producing carboxylic acids, alcohols, and/or aldehydes (Kleiser and Frimmel 2000). Olefins, amines, or activated aromatic compounds react quickly with ozone; however, aliphatic carbon moieties, amides, and nitroso compounds have low reactivity towards ozone, and are therefore not effectively oxidised (Lee et al. 2007a).

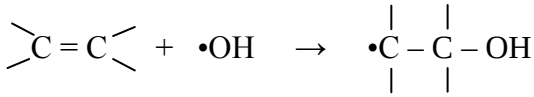
Ozonation transforms high MW compounds into low MW compounds with little overall reduction in DOC concentration (Amy et al. 1988), but the process is eminently suitable for combining with BAC for NOM removal. It has been reported that direct ozone reactions are mainly responsible for the low MW organic compound formation (Hammes et al. 2006). At typical ozone doses the carbon-carbon chains of organic matter are broken into smaller segments of highly oxidised and biodegradable DOC and assimilable organic carbon (AOC) (Takeuchi et al. 1997), and these products serve as a carbon source for bacteria. Numerous studies have shown that the application of GAC or BAC after ozonation significantly improves DOC removal, and reduces DBP formation upon final disinfection (e.g. Shukairy and Summers 1992; Carlson and Silverstein 1997; Chang et al. 2002).

1.3.7 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) usually involve the addition of a combination of chemical oxidants and/or a source of radiation, and are characterised by the in situ generation of radicals, namely hydroxyl radicals (•OH) (Sanly et al. 2007). Various forms of AOPs are currently utilised in the water industry, such as ozone/UV, ozone/H_2O_2, UV/H_2O_2, and Fenton's reactions. In each process, the pathway to •OH formation varies, however the •OH reaction mechanism with NOM is the same. There are several ways in which NOM might react with an •OH radical. It can either react via an H-atom abstraction to yield a carbon centred radical (Equation 1); by the addition of the •OH to a double bond (Equation 2); or an electron transfer reaction, where an •OH abstracts an electron from an electron rich substituent (Kleiser and Frimmel 2000).



(1)



(2)

The highly reactive carbon centred radicals produced from Equations 1 and 2 react quickly with oxygen, forming organic peroxyl-radicals which can then react amongst themselves and produce ketones or aldehydes and/or carbon dioxide (Kleiser and Frimmel 2000). Recently, Westerhoff et al. (2007) directly measured the rate

constants for reactions between •OH and NOM, obtaining values between $1 – 5 \times 10^8$ M^{-1} s^{-1} (Westerhoff et al. 2007).

The hydroxyl radicals need to be generated in relatively high steady-state concentrations in order to efficiently react with the NOM in the water (Legrini et al. 1993). The rate of the •OH oxidation of NOM depends on the type of AOP used, as different methods produce •OH at different rates (Haag and Yao 1992). The efficiency of AOPs depend upon the •OH scavenging nature of the water matrix, as DOC and carbonate/bicarbonate are important scavengers in natural waters. Oxidation of NOM is more efficient in waters with low pH and alkalinity, as •OH are not consumed by high concentrations of carbonate and bicarbonate ions (Chin and Berube 2005).

AOP processes may cause minor alterations in the NOM functional groups without causing a major breakdown of the structure, or a major breakdown of the large aromatic or long chain NOM molecule into lower molecular weight organic compounds. Not only are the functional groups, molecular structure, and the molecular weight distributions changed by these alterations, but the physico-chemical and biological characteristics of the original NOM molecules are also changed (Song et al. 2004). AOPs can completely mineralise NOM into carbon dioxide, however this complete process is not practical, as the costs are prohibitive. Partial oxidation is more feasible for water utilities. The products from AOPs are reported to be either less reactive with chlorine, forming less toxic by-products; or form easily biodegradable products which are then efficiently eliminated via BAC/AC filtration after the AOP (Toor and Mohseni 2007).

1.4 Disinfection

Disinfection is the final phase of the drinking water treatment process in many potable water systems, and a disinfectant residual is considered essential by some utilities in order to maintain the water quality throughout the distribution system. Without sufficient disinfection, there are risks of outbreaks of waterborne illnesses and pathogens, such as *E. coli*-induced gastroenteritis (Hrudey et al. 2003), and giardiasis (Odegaard and Nygard 2004). Chlorine is the most widely used disinfectant due to its broad range of biocidal effectiveness, ease of application and

control, and cost effectiveness; however, it has the disadvantage of producing relatively high concentrations of the regulated DBPs. As a result of the increasingly stringent guidelines imposed on certain DBPs, many water utilities have switched, or are in the process of switching, to alternative disinfectants, such as chloramine or ozone.

1.4.1 Chlorine

Chlorine has been in use since the early part of last century, and is the most commonly utilised disinfectant due to its efficiency and its inexpensiveness. It is a highly reactive and effective disinfectant, as shown by its high oxidising capacity (E° at 25°C = 1.49 V (Glaze 1990)). In water, chlorine hydrolyses into chloride ion and hypochlorous acid (HOCl) (Equation 3):

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad (3)$$

In turn, HOCl exists in equilibrium with hypochlorite ion (OCl^-) (Equation 4):

$$HOCl \rightleftharpoons OCl^- + H^+ \quad (4)$$

HOCl is a more potent disinfectant than OCl^-, due to its ability to easily penetrate the cell walls of microorganisms, while the negative charge of OCl^- means it cannot easily diffuse through cell walls (White 1999). Therefore, the pH of the water being treated impacts significantly on the effectiveness of chlorine as a disinfectant. As the pH of source waters is usually between 6 – 8, and the pK_a of HOCl is 7.5 at 25°C, both species are present during chlorination, with the proportion of OCl^- increasing with increasing pH (Richardson 1998; White 1999).

1.4.2 Chloramine

There are three inorganic chloramine species which can form when chlorine reacts with ammonia: monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). The chemistry can be summarised in its simplest form by three reversible reactions (Equations 5 – 7) (Diehl et al. 2000):

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O \quad (5)$$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \quad (6)$$

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O \quad (7)$$

NH_2Cl is the preferred species in drinking water disinfection, due to its relative stability and biocidal properties. Throughout this Thesis, monochloramine will be referred to as 'chloramine'. It can be generated via the addition of chlorine to water containing ammonia; addition of ammonia to water containing free chlorine residual; or the addition of preformed chloramine to water by preparation of a premixed solution of ammonia and chlorine.

Chloramine has a low oxidising potential (E° at 25°C = 0.75 V (Glaze 1990)) and is usually used as a secondary disinfectant rather than a primary disinfectant, due to its need for a longer contact time in order to inactivate pathogens. Chloramine produces low amounts of the regulated DBPs (e.g. THMs and haloacetic acids (HAAs)) in comparison to chlorine, but higher amounts of *N*-nitrosodimethylamine (NDMA), an emerging DBP which has recently been added to the Australian Drinking Water Guidelines (NRMMC-NHMRC 2011).

1.4.3 Ozone

Ozone is a powerful oxidant and has become a viable alternative to chlorine as a disinfectant. Ozone rapidly decomposes in aqueous solutions and, as a consequence, only provides a short-term residual (less than one hour) in the distribution system (Camel and Bermond 1998). A secondary disinfectant, such as chlorine or chloramine, is therefore typically added prior to distribution. It has been shown that if ozonation is applied prior to a biofiltration step, the available substrates for microbial regrowth are decreased and ozone is sufficient to provide primary disinfection, resulting in a lower disinfectant demand in the finished water; i.e., lower doses of chlorine or chloramines would be required to provide adequate residual in the distribution system (Shukairy and Summers 1992).

Ozone has the highest thermodynamic oxidation potential of the common oxidants (E° at 25°C = 2.07 V (Rice and Gomez-Taylor 1986)), however it is highly selective in its oxidation reactions (Glaze et al. 1987). The reaction schemes that determine products of ozonation of natural waters are complex and will be discussed further in Sections 2.2.1. and 4.1.1. At present, the main drawback to the use of ozone in drinking water treatment is the formation of bromate when bromide is naturally present in the water source, as is commonly the case with source waters from Western Australia (Section 1.5.1.4).

1.5 Disinfection By-Products

The nature of product mixtures formed during disinfection depends on the disinfectant used and a variety of other reaction conditions. The rate and extent of formation of the DBPs is dependent on the contact time between the disinfectant and the water; the characteristics and concentration of the NOM; the concentration of bromide and iodide ions; and the temperature and pH of the water (Singer 1994; Krasner 1999; Diehl et al. 2000; Liang and Singer 2003).

There are a number of epidemiological studies showing an association between exposure to chlorinated or chloraminated drinking water and cancers of the urinary and digestive tracts (e.g. Morris et al. 1992; Koivusalo et al. 1994), as well as several toxicological studies showing that a number of DBPs are potentially carcinogenic and can cause adverse reproductive and developmental effects (e.g. Swan et al. 1992; Magnus et al. 1999; Yang 2004). However, links between cancers and DBPs are varied and, in some cases, controversial, and studies should be interpreted with caution as they cannot prove causation, only correlation (Kristiana et al. 2012). There is, however, a broadly accepted link between bladder cancer and chlorinated water (Bull et al. 2006).

Due to the potential health risk to humans associated with DBPs in drinking water, some DBPs have been regulated within the water industry. However, care must be taken when assigning importance to some DBPs. While trihalomethanes (THMs) and haloacetic acids (HAAs) are the most thoroughly researched and regulated DBPs, it is the emerging DBPs, such as the *N*-nitrosamines or iodo-organic compounds, such as iodo-THMs (I-THMs), which are suspected to have more impact on human health

even though they are present in lower concentrations (Bull et al. 2006; Krasner et al. 2006).

1.5.1 Commonly Regulated Disinfection By-Products

1.5.1.1 Trihalomethanes (THMs)

The trihalomethanes (THMs) are the most extensively studied DBPs as they were the first group of DBPs to be found in drinking water, largely because they are far more readily detected than other DBPs. The four regulated THMs (THM4) are: chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$). These four THMs are the most frequently identified, and usually the most concentrated, DBPs found in drinking waters (Kleiser and Frimmel 2000). In the absence of bromide, chlorine (as HOCl/OCl^-) will react with NOM to form $CHCl_3$, whereas in the presence of bromide, it will oxidise bromide to hypobromous acid/hypobromite ion (HOBr/OBr^-), which will also react with NOM, resulting in a shift in THM species toward the brominated species. It is the mixture of HOCl/HOBr which leads to the formation of the four regulated THM species (Amy et al. 1991). Ozone in the presence of organic matter and bromide alone will lead to the formation of $CHBr_3$ (Cooper et al. 1986).

There have been several studies investigating the possible precursors for THM formation. For example, some of the main THM precursors have been reported to be the polyhydroxyaromatic structures in NOM (Reckhow et al. 1990; Krasner 1999), and the hydrophilic acid fraction of NOM (Marhaba and Van 2000). Other studies have suggested aliphatic carboxylic acids, hydroxybenzoic acids, phenols, and pyrrole derivatives are reactive NOM substrates for THM formation (Norwood et al. 1980; Korshin et al. 1997).

The US Environmental Protection Agency (US-EPA) regulates the sum of these four THMs (THM4) at 80 µg L^{-1} (US-EPA 2001), and the European Union (EU) regulates the THM4 at 100 µg L^{-1} (EU 1998). The Australian Drinking Water Guidelines have set the maximum level of THM4 in treated water at 250 µg L^{-1} (NRMMC-NHMRC 2011). The World Health Organisation (WHO) has set maximum regulation values (as µg L^{-1}) for each THM: $CHCl_3$: 200; $CHBrCl_2$: 60; $CHBr_2Cl$: 100; and $CHBr_3$: 100 (WHO 2008).

1.5.1.2 Haloacetic Acids (HAAs)

Haloacetic acids (HAAs) have not been studied as extensively as THMs, however many studies have reported that THMs and HAAs are the two largest classes of halogenated DBPs on a mass concentration basis in drinking water distribution systems (Krasner et al. 1989; Richardson 2003; Rodriguez et al. 2004; Krasner et al. 2006). There are nine species of HAAs which can be formed upon disinfection with chlorine or chloramine in the presence of bromide: monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), trichloroacetic acid (TCAA), and tribromoacetic acid (TBAA). The US-EPA regulates the sum of five HAAs (HAA5: MCAA, DCAA, TCAA, MBAA, and DBAA) at 60 µg L^{-1} (US-EPA 2001) based on running annual averages. The Australian Drinking Water Guidelines have set the maximum level of three HAAs, MCAA, DCAA, and TCAA, in treated water as 150, 100, and 100 µg L^{-1}, respectively (NRMMC-NHMRC 2011). The World Health Organisation (WHO) has set maximum regulation values for DCAA and TCAA as 50 and 100 µg L^{-1}, respectively (WHO 2008).

DCAA and TCAA are the most extensively studied HAAs, and they have been identified as major halogenated substances in chlorinated drinking water (Cowman and Singer 1996). DCAA is often the most predominant HAA species formed (Kanokkantapong et al. 2006). During chloramination, the dihaloacetic acids (X_2AA) have been reported to be the predominant species formed (Cowman and Singer 1996; Speitel Jr. 1999; Diehl et al. 2000), which is unfortunate as some of these species are of the most concern to human health. HAA formation from chloramination has been shown to be significantly lower than that observed from chlorination, and there is also less bromine incorporation into the HAAs in chloraminated waters compared to chlorinated waters (Cowman and Singer 1996).

There have been several studies investigating the potential precursors for HAA formation (Marhaba and Van 2000; Chang et al. 2001; Kanokkantapong et al. 2006). Functional groups which have been proposed as precursors to HAA formation are carboxylic acids, aromatic compounds, amides, amino acids, and ketones (Kanokkantapong et al. 2006).

1.5.1.3 Bromate

Bromate (BrO_3^-) is a by-product formed upon ozonation of bromide-containing waters, and has been shown to be a potent carcinogen in laboratory animals (Kurokawa et al. 1986). The upper-bound estimate of cancer potency for bromate is 0.19 per mg/kg of body weight per day, and health-based value of 2 µg L^{-1} is associated with the upper-bound excess cancer risk of 10^{-5} (WHO 2008). Bromate has been classified by the US-EPA as a probable human carcinogen (B2) (US-EPA 2006), and the drinking water regulated guideline value in the USA and Europe is set at 10 µg L^{-1} (EU 1998; US-EPA 2006; WHO 2008), and in Australia the value is 20 µg L^{-1} (NRMMC-NHMRC 2011).

Bromate formation during ozonation in the presence of bromide takes place via a combination of direct ozone reactions, and indirect reactions with •OH (von Gunten 2003a). In the first step, ozone oxidises bromide to HOBr/OBr^-, or •OH oxidises bromide to •Br. The oxidobromine radical (BrO•) is then created, when either HOBr reacts with •OH, or Br• reacts with ozone. This radical then disproportionates into BrO^- and BrO_2^-, and ozone readily oxidises BrO_2^- to form bromate. The formation of bromate can be described as two phases: the initial and the secondary. In the initial phase, the half-life of ozone is in the order of seconds, and the •OH pathway is important for the formation of bromate; while in the secondary phase, the half-life of ozone is in the order of minutes to hours, and both ozone and •OH can participate in the formation of bromate (von Gunten 2003a).

Bromate formation during ozonation can be minimised via the careful optimisation of the ozonation process. Factors such as the concentrations of bromide and ozone, alkalinity, ammonia concentration, as well as the pH at which the treatment is performed, have an effect on the formation of bromate during ozonation (von Gunten and Hoigne 1994). At present, removal of bromide from a source water prior to ozonation is not practical, and once formed, bromate is difficult and non-economical to remove. Lower ozone doses and shorter contact times, as well as the lowering of pH and addition of ammonia, can assist in bromate minimisation (von Gunten and Hoigne 1994; von Gunten 2003a). Bromate minimisation techniques will be further discussed in Chapter 5.

1.5.2 Emerging Disinfection By-Products

1.5.2.1 Haloacetonitriles (HANs)

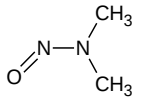
In the presence of bromide, there are nine species of haloacetonitriles (HANs) that can be formed as DBPs: chloroacetonitrile (MCAN), bromoacetonitrile (MBAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), bromochloroacetonitrile (BCAN), trichloroacetonitrile (TCAN), tribromoacetonitrile (TBAN), dibromochloroacetonitrile (DBCAN), and bromodichloroacetonitrile (BDCAN). Of these, the most commonly observed HANs in chlorinated and chloraminated waters are DCAN, TCAN, BCAN, and DBAN (Krasner et al. 1989; Yang et al. 2007).

During chlorination, HANs usually form at much lower concentrations than HAAs or THMs, however the HANs are relatively toxic and have been prioritised into a group of approximately 50 DBPs predicted to be the most carcinogenic (Woo et al. 2002; Richardson 2003; Agus et al. 2009). HANs have been found to be more cytotoxic and genotoxic than the regulated HAAs (Muellner et al. 2007), and compared to the chlorinated analogues, the brominated HANs generally exhibit higher cytotoxic and genotoxic potencies (Muller-Pillet et al. 2000; Muellner et al. 2007). HANs have also been found to be mutagenic (Bull et al. 1985; Bull et al. 2011). The carcinogenic potential of HANs has not yet been fully established, however the US-EPA has classified DCAN and DBAN into Group C as possible human carcinogens (US-EPA 2007). Only these two HANs have had regulatory guidelines set, with WHO being the only organisation to assign maximum regulation values for DCAN and DBAN at 20 and 70 μg L^{-1}, respectively (WHO 2008).

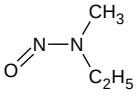
The chlorination of certain amino acids (e.g. aspartic acid, asparagine, tryptophan, kynurenine, glutamic acid and histidine) has been found to form HANs (Ueno et al. 1996; Bond et al. 2009a). Algae suspensions and nitrogen-containing humic substances have also been found to form HANs during chlorination (Oliver 1983; Reckhow et al. 1990; Ueno et al. 1996). The overall levels of HANs in chlorinated water is dependent upon the balance between their formation and degradation rates, as continuing reactions of HANs with residual chlorine can lead to a decay of HANs after formation (Reckhow et al. 1990). The effect of chloramination on HAN formation has not been extensively studied, though observations point to formation mechanisms involving monochloramine (Yang et al. 2007).

1.5.2.2 N-*Nitrosamines*

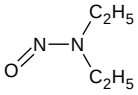
N-Nitrosamines first gained interest as emerging DBPs in 1989, when *N*-nitrosodimethylamine (NDMA) was discovered in drinking water in Ontario, Canada (Jobb 1994). Since then, *N*-nitrosamines have been detected in many waters; however this review will focus on *N*-nitrosamines in drinking waters. Nine *N*-nitrosamines are included in this review: NDMA, *N*-nitrosoethylmethylamine (NEMA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-n-propylamine (NDPA), *N*-nitrosodi-n-butylamine (NDBA), *N*-nitrosodipiperidine (NPIP), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosomorpholine (NMOR) and *N*-nitrosodiphenylamine (NDPhA) (Figure 1-1).



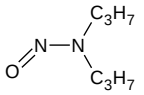
N-Nitrosodimethylamine (NDMA)



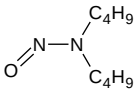
N-Nitrosoethylmethylamine (NEMA)



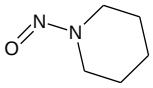
N-Nitrosodiethylamine (NDEA)



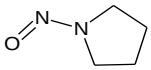
N-Nitrosodi-n-propylamine (NDPA)



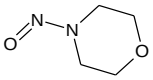
N-Nitrosodi-n-butylamine (NDBA)



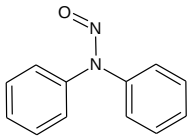
N-Nitrosopiperidine (NPIP)



N-Nitrosopyrrolidine (NPYR)



N-Nitrosomorpholine (NMOR)



N-Nitrosodiphenylamine (NDPhA)

Figure 1 - 1: Names and structures of the nine *N*-nitrosamines generally analysed in drinking water

The formation and presence of these *N*-nitrosamines in drinking water is of great concern to the water industry, as many of them have been reported to be carcinogenic, mutagenic, and/or teratogenic (O'Neill et al. 1984; Loeppky and Micheljda 1994). NDMA and NDEA have been identified by the US-EPA Integrated

Risk Information System (IRIS) as probable human carcinogens, and the other *N*-nitrosamines, with the exception of NDPhA, have been identified as possible carcinogens (US-EPA 2008). It has been reported that the carcinogenic properties of this group decrease with an increase in the length of the aliphatic chain, with the exception of NDEA, which is reported to be less toxic than expected (Andrzejewski et al. 2005). The US-EPA has added NDMA, NEMA, NDEA, NDPA, NDBA, and NPYR to the Unregulated Contaminant Monitoring Rule 2 (UCMR-2) (US-EPA 2005).

Several countries have adopted guideline values for some of the *N*-nitrosamines. In Canada, Health Canada has a Maximum Acceptable Concentration (MAC) of 40 ng L^{-1} for NDMA (HC 2011), while the Ontario Ministry of the Environment (MOE) has issued an Interim MAC of 9 ng L^{-1} (MOE 2002). In the United States, the California Department of Public Health has established a notification level of 10 ng L^{-1} each for NDMA, NDEA, and NDPA (CDPH 2007). The World Health Organisation (WHO) has included a drinking water guideline value of 100 ng L^{-1} for NDMA (WHO 2008), and this is also the health guideline value recently adopted in the new Australian Drinking Water Guidelines (NRMMC-NHMRC 2011).

The most studied *N*-nitrosamine is NDMA. In drinking water, the compound is reportedly found primarily in water distribution systems that use chloramination as the disinfectant (Najm and Trussell 2001; Choi and Valentine 2002a), though NDMA formation has also been reported during treatment with chlorine (Mitch and Sedlak 2002; Zhao et al. 2008). Charrois et al. (2004) were the first to report *N*-nitrosamines other than NDMA in drinking water systems when they observed the occurrence of NPYR and NMOR in addition to NDMA in a surface water (DOC: 16 mg L^{-1}) which had been chloraminated in combination with UV treatment.

The formation of *N*-nitrosamines generally involves reaction between inorganic nitrogen-containing species (such as monochloramine or dichloramine) with organic nitrogen species. Secondary aliphatic amines (for example, dimethylamine, which is the most commonly used model precursor for NDMA formation) are the most well-known organic nitrogen precursors (Mitch and Sedlak 2002; Choi and Valentine 2002a). Precursors such as dimethylamine are reported to form *N*-nitrosamines

through reaction with dichloramine via a chlorinated unsymmetrical dimethylhydrazine (UDMH) intermediate (Schreiber and Mitch 2006). The nitrosating agent dinitrogen tetraoxide (N_2O_4) is also reported to form *N*-nitrosamines when chlorination occurs in the presence of nitrite (Schreiber and Mitch 2007); and the fungicide tolylfluanid degrades into the metabolite *N*,*N*-dimethylsulfamide, which can reportedly form NDMA upon ozonation (Schmidt and Brauch 2008).

The *N*-nitrosamines will be discussed further in Chapter 3.

1.5.2.3 Iodo-trihalomethanes (I-THMs)

At present, only the chlorinated and brominated THMs are regulated, however iodinated species can also form when naturally occurring iodide (I^-) is present in source waters. When oxidised by a disinfectant (e.g. chlorine, chloramine, ozone), HOI is formed, which can then react with NOM in competition with HOCl and HOBr, such that one or more iodine atoms can become incorporated into a THM by-product. In the presence of iodide, it is thus possible to form six THMs in addition to the four regulated THMs: bromochloroiodomethane ($CHBrClI$), dibromoiodomethane ($CHBr_2I$), bromodiiodomethane ($CHBrI_2$), dichloroiodomethane ($CHCl_2I$), chlorodiiodomethane ($CHClI_2$), and iodoform (CHI_3).

I-THMs have been reported in both chlorinated and chloraminated drinking water (Hansson et al. 1987; Cancho et al. 2000; Bichsel and von Gunten 2000a). However, the concentrations of these I-THMs are typically low compared to the regulated THMs. I-THMs have low sensory threshold concentrations, with the taste and odour concentrations of iodoform being 5 and 0.02 µg L^{-1}, respectively (Cancho et al. 2000). Therefore, previous studies of their formation and their presence in treated waters have focused on their propensity to cause off-flavour issues (Hansson et al. 1987; Cancho et al. 2000). However, it has recently been found that iodinated DBPs may be more toxic than their brominated and chlorinated analogues (Richardson 2003), and this has promoted renewed interest in the occurrence and formation of I-THMs in drinking water.

In bench- and plant-scale studies, it has been reported that I-THM concentrations can be higher in chloramination than chlorination, especially if the ammonia is added before the chlorine (Hansson et al. 1987; Bichsel and von Gunten 2000a; Krasner et al. 2006). $CHCl_2I$ has been reported to be the most common I-THM observed, even in waters that contained average concentrations of bromide (Krasner et al. 2006). Investigations into the effect of ozonation on I-THMs has shown that I-THMs do not form as a result of ozonation (Bichsel and von Gunten 2000a), and that ozonation effectively oxidises pre-formed I-THMs (Bichsel 2000).

The I-THMs will be discussed further in Chapter 6.

1.6 Scope of the Study

As Australia and other countries face increasing challenges for potable water supply, such as climate shifts, expanding populations, and drought, challenges which have already resulted in scarcity of water in many urban and regional centres in Australia, water of more marginal quality must be utilised for potable purposes. Lower quality waters may contain high concentrations of organic and inorganic matter, resulting in a high degree of difficulty for the application of treatment processes. The formation of DBPs during drinking water treatment and disinfection, as well as within a distribution system, is a potentially serious public health issue, and there is a requirement to control and minimise DBP formation.

The broad aims of the studies in this Thesis were to investigate the formation of DBPs, and the effect of pre-treatment and disinfection on mechanisms of their formation. The specific DBPs studied were the four regulated THM species (THM4: $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$), the six unregulated I-THM species ($CHBrClI$, $CHBr_2I$, $CHBrI_2$, $CHCl_2I$, $CHClI_2$, and CHI_3), the nine HAA species (HAA9: MCAA, MBAA, DCAA, DBAA, BCAA, TCAA, TBAA, BDCAA, and DBCAA), five of the HAN species (HAN5: MCAN, MBAN, DCAN, DBAN, and TCAN), eight of the *N*-nitrosamines (NDMA, NEMA, NDEA, NDPA, NDBA, NPIP, NPYR, and NMOR), bromate (BrO_3^-), and iodate (IO_3^-).

The Thesis commences with an introduction to AOPs as NOM removal/transformation processes, and a discussion of a portable water treatment rig

which was designed and constructed in this project for the purpose of future on-site and laboratory investigations (Chapter 2). In Chapter 3, a study of chlorination *vs.* chloramination of a Western Australian surface water is presented, in which the resulting THM, HAA, HAN, and *N*-nitrosamine formation are discussed. In Chapters 4 – 6, the effect of the addition of an ozonation step at a Western Australian Groundwater Treatment Plant is discussed, focusing on formation of the regulated THMs and bromate (Chapters 4 and 5), and I-THM formation (Chapter 6). Finally, Chapter 7 presents the overall conclusions reached by this study, as well as recommendations for further studies.

Chapter 2

DESIGN OF A PORTABLE WATER TREATMENT RIG FOR ON-SITE TESTING OF ADVANCED OXIDATION AND BIOFILTRATION PROCESSES

2.1 Introduction

The most effective approach to reducing the formation of potentially harmful DBPs is to remove the DBP precursors prior to disinfection and distribution of the water. Oxidation and advanced oxidation processes (AOPs) have the potential to transform these precursors into partially oxidised compounds which are generally less reactive with chlorine or chloramine (Amy et al. 1991). AOPs are processes which usually involve the addition of a combination of chemical oxidants and/or a source of radiation, resulting in the in situ production of highly oxidative hydroxyl radicals (•OH) (Sanly et al. 2007). As one of the most powerful oxidising species after fluorine (Legrini et al. 1993), the •OH is non-selective and is able to oxidise compounds that cannot be easily oxidised by conventional oxidants.

The application of AOPs has been primarily focused on the removal of micropollutants and contaminants from water sources (Ma and Graham 1999; Fukushima and Tatsumi 2001; Baus et al. 2005), wastewater (Chamarro et al. 2001; Gong et al. 2008), and industrial effluent (Ledakowicz and Gonera 1999; Azbar et al. 2004; Acar and Ozbelge 2006; Catalkaya and Kargi 2007). However, AOPs have also recently been shown to have potential as treatment methods focused on NOM removal (Goslan et al. 2006; Lamsal et al. 2011). One attraction of AOPs for the water treatment industry is their potential to completely oxidise or mineralise organic contaminants through a process which operates at near ambient temperature and pressure (Matilainen and Sillanpaa 2010).

2.2 (Advanced) Oxidation Treatment Processes

Oxidants can be dosed at different stages of a treatment process, depending on the purpose of the oxidant. In broad terms, these stages are: pre-oxidation, intermediate oxidation, or final disinfection (Camel and Bermond 1998). The usual aims of a pre-oxidation step are to eliminate mineral compounds (i.e. oxidation of reduced substances, such as NH_3, H_2S, Fe(II) and Mn(II)), colour and turbidity, and taste and odour compounds. The step generally enhances coagulation and flocculation, and also partially degrades NOM and inactivates micro-organisms. Intermediate oxidation degrades toxic micropollutants, removes DBP precursors (e.g. THM precursors), and increases biodegradability. The increase in biodegradability can

greatly enhance removal of organic material upon subsequent treatment (e.g. biological activated carbon (BAC) filtration). Final disinfection should result in the inactivation of all the remaining micro-organisms and, due to the combined oxidation-BAC treatment, subsequent DBP formation should be minimised (Camel and Bermond 1998).

This Chapter will focus on AOPs which were included in the design of a water treatment rig in conjunction with industry partners (ozone, peroxide, UV, ferrate^{VI}, and (photo-) Fenton's reagent) and combinations of these AOPs. Only the transformation of NOM and reduction of DBP formation potential related to drinking water sources will be reviewed here.

2.2.1 Ozone

Ozone is used for both disinfection and oxidation within the drinking water industry, as discussed in Sections 1.3.5 and 1.4.3. The decomposition of ozone in water is complex and can be described as a series of initiation, promotion, and inhibition reactions. Decomposition is initiated by hydroxide (OH^-), the deprotonated form of hydrogen peroxide (HO_2^-), and some organic moieties within NOM, all of which then induce the formation of •OH (Equations 1 – 4) (Staehelin and Hoigne 1982; von Gunten 2003b). If the •OH reacts with NOM and superoxide radicals (e.g. $•HO_2/•O_3/•O_2^-$) are produced (e.g. Equations 5 and 6), these can then form more •OH (Equations 7a – 8b) (von Gunten 2003b).

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (1)$$

$$O_3 + HO_2^- \rightarrow •OH + •O_2^- + O_2 \quad (2)$$

$$O_3 + •O_2^- \rightarrow •O_3^- + O_2 \quad (3)$$

$$O_3 + •OH \rightarrow HO_2• + O_2 \quad (4)$$

$$•OH + NOM \rightarrow •NOM + H_2O \text{ or } •NOM + OH^- \quad (5)$$

$$•NOM + O_2 \rightarrow NOM\text{-}•O_2 \rightarrow NOM^+ + •O_2^- \quad (6)$$

$pH < \approx 8$

$$•O_3^- + H^+ \rightleftharpoons •HO_3 \quad (7a)$$

$$•HO_3 \rightarrow •HO + O_2 \quad (7b)$$

$$pH > \approx 8 \qquad \bullet O_3^- \rightleftharpoons \bullet O^- + O_2 \qquad (8a)$$

$$\bullet O^- + H_2O \rightarrow \bullet HO + OH^- \qquad (8b)$$

The chain reaction ceases when the •OH is scavenged by an inhibitor (e.g. carbonate or NOM), which does not release superoxide to accelerate ozone decomposition. While ozone decomposition results in •OH formation, the concentration of radicals present at any given time is very low compared to the concentration of •OH in the use of AOPs (Kleiser and Frimmel 2000).

The kinetics of the direct oxidation by ozone depends on the presence of electron-rich reactive moieties in organic molecules, such as olefins, activated aromatic systems, and deprotonated amines, which react fast with ozone, whereas many other moieties have intermediate to low reactivity with ozone (Hoigne and Bader 1983a; Hoigne and Bader 1983b). It is these low reactivity compounds (e.g. aldehydes, ketones, and carboxylic acids) which tend to accumulate as oxidation products from the reaction of ozone with NOM (von Gunten 2003b). Under normal drinking water conditions (1 – 5 mg/L applied ozone dose; 5 – 20 minutes contact time), organic compounds are usually only partially oxidised, and while ozone is capable of completely oxidising many organic compounds to CO_2 and H_2O, a large dose of ozone is usually required (> 3 M O_3/M organic compound) in addition to a long reaction time (sometimes hours) (Rice and Gomez-Taylor 1986).

It is increasingly common for ozone to be used as a pre-oxidant or intermediate oxidant during drinking water treatment. The ozonation of waters containing NOM results in formation of biodegradable by-products, which are a carbon source for bacteria, resulting in greater potential for regrowth problems in distribution systems, and lowering the water quality. Therefore, the process is usually coupled with a biological filtration step, in order to remove the biodegradable organic matter prior to final disinfection. There have been several studies investigating the efficiency of DOC removal (Siddiqui et al. 1997; Nishijima et al. 2003) via transformation of DOC to BDOC (Kim et al. 1997; Griffini et al. 1999) and subsequent removal of BDOC using BAC. The extent of DOC removal depends on the content of ozone-reactive DOC within the water source. Multi-stage ozonation followed by biofiltration has been reported to enhance DOC removal, as the ozone is able to

attack the refractory DOC rather than be consumed by the newly formed BDOC (Nishijima et al. 2003). The behaviour of the source water should always be assessed with regard to the application of the ozone-biofiltration scheme, as some waters have been found to not produce biologically stable water and require further pre-treatment (Franzmann et al. 2000). Also, bromate formation during the ozonation of bromide-containing waters is a drawback to the ozonation-biofiltration scheme, as bromate is not removed during the biofiltration step (Siddiqui et al. 1997). An early study showed that ozone oxidation followed by chlorination can result in increased levels of trihalomethanes (THMs), which can be partially attributed to the formation of aldehydes by ozonation (Trussell and Umphres 1978). In contrast, several more recent studies have shown that the formation potentials (under chlorination conditions) of DBPs, such as THMs, haloacetic acids (HAAs), and *N*-nitrosodimethyamine (NDMA), decrease upon pre-ozonation (e.g. Siddiqui et al. 1997; Galapate et al. 2001; Chang et al. 2002; Lee et al. 2007b), due to the transformation of reactive DBP precursors to less reactive moieties. The more reactive hydrophobic and aromatic DOC has been shown to transform into less reactive hydrophilic DOC (Galapate et al. 2001). There is reported to be a decrease in the extent of aromatic organic compounds, particularly in phenolic-OH such as those found in resorcinol or meta-dihydroxy benzene ring structures (Galapate et al. 2001; Chang et al. 2002), functional groups which are known to form THMs in high yields.

2.2.2 UV Photolysis/Photooxidation

Like ozone, UV-photolysis/photooxidation (UV) is used widely for disinfection purposes. Compared to other NOM or contaminant removal processes, the UV processes do not require any substrates to be recycled, no chemical addition is needed, and no sludge by-products are formed (Parkinson et al. 2003). Several studies have compared the effects of UV-A (300-400 nm), UV-B (260-340 nm), UV-C (254 nm), and vacuum-UV (VUV, 185 nm) on NOM in source waters (e.g. Parkinson et al. 2003; Debrovic et al. 2007).

In UV processes, the target compounds interact with natural or artificial light, which induce a series of photochemical reactions (Frimmel 1994). Photons are absorbed by UV-absorbing functional groups or chromophores in the NOM (e.g. aromatic and

other conjugated unsaturated moieties; Equation 9), and this can then result in indirect photooxidation where energy/electrons are transferred to components (e.g. oxygen) from the excited chromophore (Equation 10), and/or direct phototransformation where chromophores are degraded to non-UV absorbing components (Legrini et al. 1993; Parkinson et al. 2003).

$$\mathrm{NOM} \xrightarrow{h\nu} \mathrm{NOM}^* \quad (9)$$

$$\mathrm{NOM}^* + \mathrm{O_2} \rightarrow \bullet\,\mathrm{NOM}^+ + \bullet\,\mathrm{O_2}^- \quad (10)$$

The excited species (photoreactants) are then able to react with NOM to form transient organic radical species, and these then degrade the UV and non-UV absorbing components, eventually mineralising them to CO_2 (Parkinson et al. 2003). The photoreactants include singlet oxygen ($^1O_2$), peroxy radicals (ROO•), H_2O_2 (which then produces •OH), solvated electrons (e^-_{aq}), superoxide anions ($\bullet O_2^-$) and humic structures (^{3}NOM*) excited to the triplet states (Hoigne et al. 1989; Frimmel 1994).

UV photolysis has been shown to change the chemical and biological properties of NOM, such as the molecular weight (MW) distribution, DOC/TOC concentrations, UV_{254} absorbance, and bacterial regrowth potential (BRP) (Frimmel 1998; Kleiser and Frimmel 2000; Thomson et al. 2002; Parkinson et al. 2003; Buchanan et al. 2005; Goslan et al. 2006). However, it should be noted that any significant reductions in NOM concentrations observed occurred under much higher UV doses than those typically employed in drinking water treatment for disinfection purposes (e.g. Thomson et al. 2002; Buchanan et al. 2005). In comparison, UV irradiation performed at typical disinfection doses resulted in negligible alteration to the overall NOM concentration (Chin and Berube 2005). Several studies have shown that photooxidation of NOM resulted in the formation of low molecular weight by-products (Frimmel 1998; Parkinson et al. 2003; Goslan et al. 2006). The effectiveness of the UV process is dependent on the ability of the compounds to absorb the emitted light, and is enhanced when UV is combined with hydrogen peroxide (see Section 2.2.3) or ozone (see Section 2.2.4).

The vacuum-UV (VUV) process involves irradiation at 185 nm, and is based on the photochemically initiated homolysis of water, resulting in the generation of •OH and hydrogen atoms. The overall efficiency of the VUV oxidation process can be limited by the relatively high absorption cross-section of water in the VUV part of the spectrum (Debrovic et al. 2007). As the lifetimes of the radicals generated by the process are short, they cannot diffuse far outside the irradiated area, which then leads to the formation of areas within a reactor which are rich in radicals but depleted in organic matter, resulting in extreme heterogeneity between the irradiated and non-irradiated areas (Debrovic et al. 2007). For this reason, VUV is not generally used in water treatment applications and it was not included in the design of the water treatment rig.

2.2.3 UV/Hydrogen Peroxide

The combination of UV and hydrogen peroxide results in the photocatalytic dissociation of H_2O_2 to yield •OH (Legrini et al. 1993; Rosenfeldt et al. 2006), thereby increasing the effectiveness of the disinfection and oxidising potential. It has been reported that the degradation of target compounds can occur approximately 8 times more effectively with UV/H_2O_2 than UV alone (Debrovic et al. 2007; Bond et al. 2009b). However, it is important to optimise the UV/H_2O_2 process and obtain the correct proportion of UV irradiation and H_2O_2 dose, as it has been found that excess H_2O_2 acts as an •OH scavenger, thereby resulting in a less efficient process (e.g. Wang et al. 2000; Wang et al. 2001; Tuhkanen 2004).

The commercial UV/H_2O_2 systems which are currently employed in drinking water treatment systems to remove trace organic contaminants operate at conditions in which NOM is partially oxidised (Sarathy and Mohseni 2007). Although the mineralisation of NOM is low under these conditions, there are significant changes in the structural characteristics of the NOM. It has been reported that the •OH generated by UV/H_2O_2 preferentially reacts with high MW NOM, resulting in an increase in lower MW NOM which is generally more biodegradable (Wang et al. 2006; Sanly et al. 2007; Sarathy and Mohseni 2007). Although the UV/H_2O_2 treatment has been found to decrease the formation potential of some DBPs, it has been reported to increase the formation potential of others. Zhao et al. (2008) found that UV/H_2O_2 treatment of two source waters (a lake and river water with total organic carbon

(TOC) concentrations of 5.7 and 23.9 mg L^{-1}, respectively) can result in higher concentrations of NDMA compared to the untreated source water and treatment of the source water with UV alone.

2.2.4 Ozone/UV

Compared to O_3/H_2O_2 and UV/H_2O_2, the O_3/UV process provides the maximum yield of •OH per oxidant (Gottschalk et al. 2000). The •OH are produced via the photolysis of aqueous ozone, directly yielding H_2O_2 (Equation 11), which then, along with ozone, participates in secondary reactions forming the hydroxyl radicals (e.g. Equation 12) (Peyton and Glaze 1988).

$$O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_2 \quad (11)$$

$$H_2O_2 \xrightarrow{hv} 2\ \bullet OH \quad (12)$$

The effectiveness of the ozone/UV system is influenced by the order in which the reactants are combined. Paillard et al. (1987) found that the best technique was to apply the ozone directly into the UV chamber, and that the ideal radiation strength was the lowest rate at which the dissolved ozone is entirely consumed. The efficiency of the system varied according to the type of organic compound in the water, as well as the pH, alkalinity, and the rate of ozonation and radiation power (Paillard et al. 1987).

Chin and Berube (2005) performed laboratory scale batch O_3/UV experiments on reservoir water taken over several months (average TOC: 1.8 mg L^{-1}), and observed a significant reduction in NOM concentration (50% TOC mineralised after 60 mins), as well as a reduction in THMFP and HAAFP upon chlorination (approximately 80% and 70%, respectively). The reductions in THM and HAA precursors were attributed to the conversion of the organic precursors into forms that are not reactive with chlorine to produce these DBPs. Several other researchers have also observed significant reductions in THMFP during treatment with O_3/UV compared to ozone alone (Glaze et al. 1982; Peyton et al. 1982; Backlund 1994; Amirsardari et al. 2001). However, care must be taken to optimise the process, as low doses can enhance the chlorine consumption and THMFP (Backlund 1994).

2.2.5 Ozone/Hydrogen Peroxide

The addition of H_2O_2 to ozone is otherwise known as peroxone. It is a common AOP, as the addition of H_2O_2 is the cheapest and easiest way to convert the conventional method of ozonation into an AOP. Ozone decomposition is greatly accelerated, promoting the formation of •OH. Hydrogen peroxide initiates the decomposition of the ozone via the formation of a hydroperoxide ion (HO_2^-) (Acero and von Gunten 2001). This then attacks the ozone, and the result is one •OH per decomposed ozone molecule (Staehelin and Hoigne 1982).

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad (13)$$

$$O_3 + HO_2^- \rightarrow \bullet OH + \bullet O_2^- + O_2 \quad (14)$$

Treatment using O_3/H_2O_2 is recommended for water in which ozone is stable (i.e. low pH, high alkalinity, as well as content and type of NOM), and therefore degrades slowly (Rosenfeldt et al. 2006). Acero and von Gunten (2001) found that with increasing H_2O_2/O_3 ratio, the ozone exposure decreased and •OH exposure increased, and that, above a ratio of 0.19, additional H_2O_2 did not further increase the •OH exposure.

Studies have shown that the addition of O_3/H_2O_2 enhances DOC reduction when compared to ozone alone (Fahmi et al. 2003; Irabelli et al. 2008). Irabelli et al. (2008) performed a peroxone pilot scale study over several months on a river water, and reported that, when ozone was applied prior to H_2O_2 addition, there was better NOM removal compared to when H_2O_2 was applied first (61% and 53% DOC removal, respectively). However, treatment by both O_3/H_2O_2 and H_2O_2/O_3 resulted in higher THM formation upon disinfection with chlorine than treatment by ozone alone, and the treated waters required a higher chlorine dose to attain the same 20 minute chlorine residual compared to water treated by ozone alone (Irabelli et al. 2008). Fahmi et al (2003) investigated single and multi-stage O_3/H_2O_2 followed by biological treatment of a reservoir water. Single stage treatment (60 mins oxidation, followed by biological treatment) of the reservoir water resulted in DOC removal of 62% and 40%, using O_3/H_2O_2 and ozone alone, respectively. In comparison, the

multi-stage O_3/H_2O_2 treatment (4 times repetition of 15 min ozonation with H_2O_2, followed by biological treatment) resulted in 79% DOC removal (Fahmi et al. 2003).

2.2.6 Ferrate^{VI}

Due to its strong oxidising properties, interest is growing in the use of ferrate^{VI} (FeO_4^{2-}) as a water treatment chemical for oxidation/disinfection and coagulation processes, with most research focused on its use in the treatment of wastewater (e.g. Jiang and Lloyd 2002; Lee et al. 2009). Potassium ferrate (K_2FeO_4) is the best known form of ferrate^{VI}, and is considered to be an environmentally friendly oxidant in natural waters due to its non-toxic decomposition products, Fe(III) ions and ferric hydroxide (Sharma 2002). The potential applications of ferrate^{VI} in drinking water treatment may be significant due to the multi-functional nature of the reagent. In their review, Jiang and Lloyd (2002) stated that ferrate^{VI} can be used in a single dosing and mixing unit process, as the reduced ferrate^{VI} (Fe(III) ions and ferric hydroxide) simultaneously generates a coagulant during the oxidation/disinfection process. Ferrate^{VI} is able to inactivate microorganisms, partially degrade and/or oxidise organic and inorganic impurities, and remove suspended/colloidal particulate materials due to its strong oxidising potential and simultaneous generation of ferric coagulating species (Jiang and Lloyd 2002). Several studies have demonstrated the simultaneous use of ferrate^{VI} as an oxidant, disinfectant, and coagulant in drinking waters and wastewaters (e.g. Jiang et al. 2001; Yuan et al. 2002; Lee et al. 2003)).

Under acidic conditions (pH < 2), ferrate^{VI} ions have a greater redox potential (2.2 V) than ozone (2.0 V) and are the strongest of all the oxidants/disinfectants practically used for water and wastewater treatment (Jiang and Lloyd 2002). In wastewater, treatment ferrate^{VI} has the ability to rapidly oxidise nitrogen- and sulphur-containing contaminants (e.g. thiols and hydrazines) into non-hazardous products; inactivate several types of bacteria and viruses; and is an efficient coagulant for removing various toxic metals and non-metals after oxidation (e.g. Schink and Waite 1980; Bartzatt et al. 1992; Jiang and Lloyd 2002; Sharma 2002; Lee et al. 2003; Lee et al. 2005). In the case of drinking water treatment, Jiang et al. (2001) compared ferrate^{VI} and ferric sulphate as coagulation agents, and reported that ferrate^{VI} performed better than ferric sulphate at doses < 2 mg L^{-1} as Fe, effectively removed NOM (measured as UV_{254}), killed total coliforms (100%), and resulted in

low residual iron concentrations and THMFP. While investigating the assimilable organic carbon (AOC) formation from five oxidants, including ferrate^{VI}, Ramseier et al. (2011) found the application of ferrate^{VI} to a lake water (3.8 mg L^{-1} DOC) led to elevated AOC concentrations, and that the presence of cyanobacteria (*A. gracile*) increased the AOC due to cell lysis. This investigation shows the importance of the application of a post-ferrate^{VI} AOC reduction methods (e.g. BAC) if ferrate^{VI} is applied in drinking water treatment.

Although ferrate^{VI} is promising for use in water treatment, the challenge lies in the implementation of a cost-effective method to produce the amounts of ferrate^{VI} required for full-scale water treatment. Ferrate solutions are generally unstable, and stable solid ferrate salts are costly and time consuming to make (Jiang and Lloyd 2002). Recently, Jiang et al. (2009) reported the online preparation and use of ferrate^{VI} on a pilot scale at a UK wastewater treatment plant. Ferrate^{VI} was successfully electrochemically generated in situ and applied directly for wastewater treatment (Jiang et al. 2009).

2.2.7 Fenton's Processes

The conventional Fenton's process (also known as the 'dark' process) involves the application of an oxidising agent (usually H_2O_2) and a metal catalyst (metal salt or oxide, usually iron) (Matilainen and Sillanpaa 2010), while the Photo-Fenton's process involves the addition of irradiation with natural or artificial light. During the 'dark' Fenton's reaction •OH are generated via the degradation of H_2O_2 and oxidation of the metal catalyst, (e.g. Fe(II) or Fe(III)) (Voelker and Sulzberger 1996).

$$H_2O_2 + Fe^{2+} \rightarrow \bullet OH + OH^- + Fe^{3+} \quad (15)$$

During the Photo-Fenton's process (UVA/Fe(III)/H_2O_2), both the irradiation of Fe(III) and the reaction of the formed Fe(II) with H_2O_2 produces •OH, thereby resulting in increased •OH concentration and oxidation rates compared to the 'dark' process (Zepp et al. 1992; Parsons 2004).

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + \bullet OH + H^+ \quad (16)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \quad (17)$$

The regeneration of the consumed Fe(II) ions via irradiation is an advantage as one Fe(II) ion can produce many •OH, rather than the single radical produced in the 'dark' reaction, and this allows for the minimisation of the initial metal catalyst concentration (Ruppert et al. 1993).

The rates of Fenton's reactions depend on the metal catalyst concentration, as well as the H_2O_2 concentration, which controls the degradation efficiency (Chamarro et al. 2001). As with other AOPs which utilise H_2O_2, the scavenging effect of H_2O_2 results in the degradation rate depending on the H_2O_2 concentration. In addition, the Fe(II) can also scavenge •OH, therefore the Fenton's processes must be carefully optimised to maximise efficiency. When the amount of H_2O_2 is less than the Fe(II) concentration on a molar basis, chemical oxidation proceeds; however when the amounts are reversed, chemical coagulation tends to take place (Neyens and Baeyens 2003). The coagulation capability of Fenton's reagent depends on the pH, and is due to the reaction of hydroxide ions to form ferric hydroxo complexes (e.g. $[Fe(H_2O)_5OH]^{2+}$), and as a result suspended solids are captured and precipitated (Neyens and Baeyens 2003).

The main disadvantages associated with Fenton's processes are: the formation of an iron sludge after the process is complete, which is required to be disposed of appropriately; and the strict control of pH, with pH adjustment usually required before and after the treatment (Wadley and Waite 2004). The Fenton's reaction has been reported to have maximum catalytic activity at pH 2.0 – 3.0 (Pignatello 1992), due to the ferric ion precipitating as ferric hydroxide at higher pH, and the inhibition of the complexation of Fe(III) with H_2O_2 at lower pH (Pulgarin and Kiwi 1996). When Fenton's processes have been utilised in the treatment of commercial humic substances and NOM-rich waters, a pH of 4 – 5 was commonly applied (Goslan et al. 2006; Park and Yoon 2007; Sanly et al. 2007; Moncayo-Lasso et al. 2008). However, it has been reported that there is little difference in the high removal efficiencies for UV_{254} absorbance and DOC within the pH 3 – 7 range (Murray and Parsons 2004; Goslan et al. 2006). The ability to perform Fenton's processes at natural water pH is advantageous and cost-effective for water utilities, as no pH adjustment is necessary.

It has been reported that up to 90% DOC removal can be achieved using Fenton's reaction jar tests or a photo-Fenton's bench-scale reactor (Murray and Parsons 2004; Goslan et al. 2006; Sanly et al. 2007), and that the removal is efficient across the whole range of molecular weights (Sanly et al. 2007). Sanly et al. (2007) found that when the H_2O_2/Fe(III) molar ratio was less than 10, both the reaction rate and removal efficiency increased with an increase in the ratio, and when the molar ratio was above 10, the removal efficiency no longer increased. The dependency of the degradation rate on the H_2O_2 concentration can be explained by two factors: firstly, there is the significant •OH scavenging effect of H_2O_2 at higher H_2O_2 concentrations; and secondly, the decomposition rate of H_2O_2 decreases at higher H_2O_2 concentrations, resulting in a decrease in the concentration of •OH available for the degradation process (Wang et al. 2001). In their study of photo-Fenton's using solar radiation, Moncayo-lasso et al. (2008) found the TOC decreased by 70 – 90% and that when slow sand filtration was applied after the photo-Fenton's reaction and prior to chlorination, the NOM removal was almost complete, an outcome which would significantly reduce THM formation upon disinfection.

2.3 Scope of the Study

The most commonly used experimental methods for investigation of oxidative and AOP methods are small-scale experiments, such as batch/semi-batch experiments, or jar tests. These methods require synthetic water samples to be prepared, using commercially available humic or fulvic materials, or quantities taken from water sources or full-scale water treatment facilities. Often these experiments can only facilitate small amounts of sample at a time, and if large-scale research is required, the pilot system often needs to be located on-site, which requires costly infrastructure.

In order to study oxidation methods and AOPs for the removal of NOM and to assess the removal of DBP precursors, a novel water treatment rig incorporating the capacity to use several oxidation and AOP methods (ozone, peroxide, UV, ferrate^{VI}, and photo-Fenton's reagent) was designed and constructed. The rig was designed in a continuous flow configuration at a laboratory scale. The aim was to retain as much portability as possible, with flexibility to simulate plant conditions as closely as practicable. The rig also has options to include a biological activated carbon (BAC)

filter, as well as a physical filter (0.1 μm) to remove particles formed during the oxidation reactions. The design included portability to allow for testing of a variety of source waters on-site, eliminating the need for transport and storage of large volumes of raw water samples. The rig was designed to be used in this project to study the transformation of NOM in water samples by various AOP methods, in various combinations, with the overall goal of the removal of DBP, particularly emerging DBP, precursors. The information gained from the rig experiments was to be used to develop optimal treatment methods to minimise DBP formation in water treatment processes. Unfortunate circumstances meant that the final stages of the rig construction could not be completed and so the rig was not available for use during this PhD study, however the description of the design of the water treatment rig, including the rationale for key design features, is detailed in this Chapter.

2.4 Design of the Water Treatment Rig

2.4.1 Introduction

The water treatment rig was designed with the capability to interchange and vary the order of different oxidation processes, as well as having the option of applying processes in combination. Ozone (O_3), hydrogen peroxide (H_2O_2), ultra-violet irradiation (UV), ferrate (Fe(VI)), and photo-Fenton's reagent were included in the design, with the additional options of a cartridge filter and a biological activated carbon (BAC) filter. The design and construction of the rig was led by the present author, in consultation with various Partner Organisations on the ARC Linkage project (LP0882550), namely the engineering consultants GHD Pty Ltd, the local water utility (Water Corporation of Western Australia), and Professor Urs von Gunten (Eawag, Switzerland), as well as the CSIRO Scientific Engineering Unit, Waterford. The design of the rig involved numerous discussions, led by the present author, regarding which processes would be beneficial to include in the rig, as well as the best order in which they should be placed on the rig during the preparation of design drawings. The present author had a lead role during the construction of the rig, communicating the purpose and design of the rig and the various construction requirements with the manufacturers, as well as purchasing and supervising the assembly of the various parts. The design and drawings of the glass columns were devised by the present author and provided to the glassblower, and regular communication was required in order to fulfil the item requirements.

The design of the rig is discussed in Sections 2.4.2 and 2.4.3. Detailed engineering drawings, prepared by Project Partner GHD Pty Ltd, are shown in the Appendix, Figures 2-1 to 2-5.

2.4.2 Design

In order to simulate plant conditions as closely as possible, the rig was designed in a continuous flow configuration to accommodate a total sample volume of 100 L. If larger water samples were required, sample water could be pumped to and from a 1000 L bulky-box located external to the unit. A basic schematic of the design of the rig is shown in Figure 2-1.

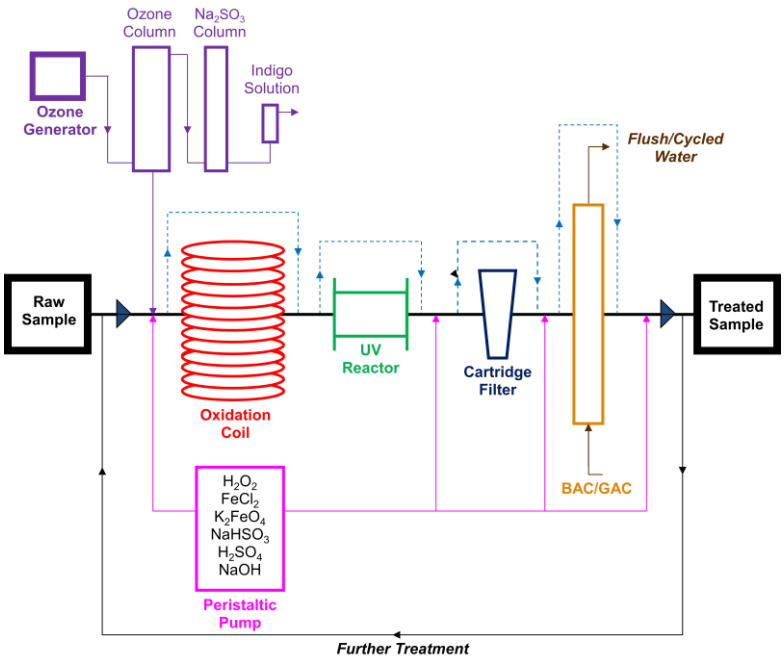


Figure 2 - 1: Basic schematic of the water treatment rig, including facilities for ozonation, hydrogen peroxide and ferrate (Fe(VI)) addition, UV irradiation, and GAC/BAC filtration

The rig was designed for maximum flexibility, such that the flow path of the sample water could be altered in order to bypass sections that were not required for a specific treatment process (indicated by perforated lines in Figure 2-1). Dosing points for acid (H_2SO_4) and alkali (NaOH) solutions were located at the beginning and end of the process, allowing for pH control. Static mixers were added at all chemical or oxidant dosing points to ensure thorough mixing of reagents with the sample.

A coil of Teflon tubing was used as the ozone reactor in preference to a batch reactor because the coil would allow for plug-flow conditions to be achieved, as opposed to a large capacity oxidation tank which would result in a dilution effect, thereby altering the oxidation potential of the system. The tubing was cut into short sections interspersed with sampling taps, allowing samples to be taken throughout the oxidation process to allow measurement of kinetic data. The lag time following H_2O_2 and/or ozone addition could be controlled by adding or removing tubing sections, allowing for the comparison of different reaction times, and simulation of variations in detention times. Ozone could not be bubbled directly into the system from the ozone generator (American Ozone Systems Inc); therefore, an additional section of the rig was designed in order to provide the main rig with ozone-enriched water. A basic schematic of the design of the additional ozone generation module is shown in Figure 2-2.

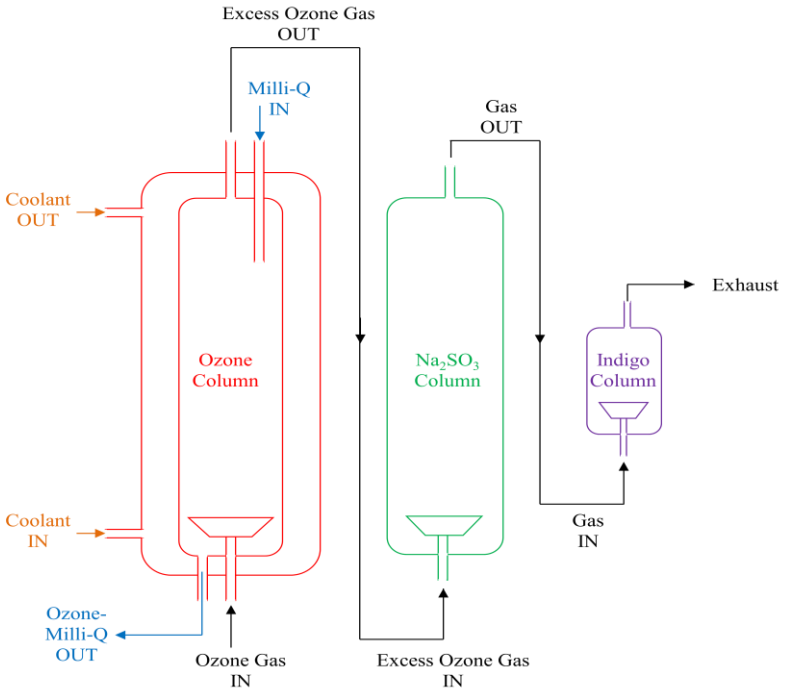


Figure 2 - 2: Basic schematic of the ozone module

Ozone will be generated and bubbled through purified water located in a purpose-made glass column, and the ozone-containing water will then be passed into the treatment system. The purified water will need to be maintained at low temperature in order to obtain maximum ozone concentrations, as the solubility of ozone in water is very low at typical ambient laboratory temperatures. Therefore, the glass column

employed an outer sleeve through which coolant could pass, connected to a recirculating cooling bath. A container of purified water (10 L) will be connected to the glass column to continuously replenish the ozone column as the ozone-enriched water is dosed into the treatment system. Two additional glass columns were attached in sequence, through which the off-gas will be bubbled. The first, larger column will contain aqueous sodium sulphite solution (1 M), in order to destroy any remaining ozone. The second, smaller column will contain blue aqueous potassium indigo trisulfonate solution (1 mM), which acts as an indicator for ozone breakthrough. When the blue solution becomes colourless, a fresh sodium sulphate solution will be required.

The UV unit comprised a commercially-available Bio-Logic ultraviolet water purifier consisting of a stainless steel chamber (0.65 L) and a low pressure lamp. Oxidants could not be applied directly into the UV unit due to its commercial design; therefore, oxidants will be applied prior to the unit and allowed to flow into the system.

The washable cartridge filter was included in the design to remove any sediment which may form during the treatment processes, in particular, coagulated particles formed during the application of ferrate or photo-Fenton's process. The activated carbon (AC) filter can be operated in an abiotic mode or as biological activated carbon (BAC). The AC filter can also serve as a medium for the removal of residual ozone or hydrogen peroxide in the treated water. The design included the option of addition of aqueous sodium bisulphite following oxidative or AOP treatment to remove any residual oxidant. Oxidants and chemicals will be stored in stainless steel vessels (2 L), to be delivered into the system by a multi-channel peristaltic dosing pump (Watson-Marlow Bredel) with 8 channels, designed to pump the low flow rates required for this purpose. The rig also has the capability to recycle previously treated water, so that multi-stage treatments can be studied.

Several sampling points are located throughout the rig, allowing samples to be collected at each oxidation stage for analysis. Chlorinated tap water or deionised water can be used to flush the system to ensure all parts of the rig, particularly the

GAC column, function efficiently. To run the AC filter in BAC mode, chlorine-free water would be used to back-flush the system.

The supporting framework was designed to enable the rig to be transportable. The ability to set up and use the rig on-site, connected directly to the water source, allows the rig to more closely simulate pilot plant conditions and limits the need to transport samples back to the laboratory, avoiding degradation or alteration of the sample water quality. The rig also has the portability and flexibility to test treatment of water from within an existing water treatment plant (e.g. AOP treatment of water taken post-clarification, prior to the filters, in a conventional flocculation/filtration plant). The various modules were fitted with forklift guides and detachable wheels so that they could be lifted off the standard-sized trailer and moved inside a building, providing the flexibility for operation of the rig in a laboratory setting, while the trailer could be stored outside the building. When taken on-site, the modules remain fully functional on the trailer. The rig layout on the trailer is shown in Figure 2-3.

Figure 2 - 3: Layout of the water treatment rig on its trailer

2.4.3 Other Issues

The design and construction of the rig was originally scheduled to take 6 to 12 months, with commissioning and optimisation of the rig to follow soon after this. Improvements to the original plans resulted in a delay in construction of several months, which was further extended when additional funds were required to budget

for some of the novel design additions to the rig. Delays were also encountered when searching for a contractor to build the rig within the tight budget constraints. The construction period was dependent on the promptness of the deliveries of the parts. The item which caused the longest delay was the specialised, purpose-made glass column for the generation of ozone-enriched water, which took almost 12 months from the time it was ordered to the time it was received.

The delays and design alterations meant that the final costs to complete the construction of the rig exceeded the budget available within the time frame of this Thesis. Photographs of the rig (Figure 2-4) show that the construction of the framework and placement of the items are complete, and all that remains is for the network of tubing to be connected. Completion of the rig should be achieved in the near future with funding from other projects.

2.5 Conclusion

The portable and flexible water treatment rig, which has been designed by the author, in collaboration with GHD Pty Ltd, Professor Urs von Gunten, CSIRO Scientific Engineering Unit, Waterford, and the Water Corporation of Western Australia, allows water samples to be treated using various oxidation and AOP methods, coupled with biological or abiotic activated carbon filtration. This will enable detailed studies of the effectiveness of these treatments in their removal of DBP precursors.

Analysis of the DOC concentration and disinfectant reactivity in the raw and treated water samples will allow determination of the DBP precursor transformation capacity of the different oxidation and AOP processes. Characterisation techniques, such as size exclusion chromatography with UV and organic carbon detection, will enable study of the character of the DOC in samples treated using different technologies and at different stages of the process. Design features, such as the variable plug-flow reactor coil and in-line static mixers, allow sufficient control of reactions for measurement of reaction rates. This will lead to improved understanding of the fundamental chemistry occurring in the treatment processes. The purpose-designed ozone generation unit allows reliable and precise dosing of ozone. Disinfection with chlorine/chloramine of the raw and treated samples and

analysis of the subsequent DBPs formed will demonstrate the capacity of the oxidative or AOP methods for DBP precursor removal.

Overall outcomes of these studies will be to develop optimal AOP treatment methods to minimise DBP formation in water treatment. The rig can also similarly be applied to the study of AOP treatment methods in water recycling processes.

Figure 2 - 4: Photographs of the water treatment rig

Chapter 3

N-NITROSAMINE AND HALOGENATED DISINFECTION BY-PRODUCT FORMATION FROM A DRINKING WATER FOLLOWING CHLORINATION AND CHLORAMINATION

3.1 Introduction

The use of disinfectants to provide microbiologically safe drinking water also leads to the formation of disinfection by-products (DBPs) through a variety of reactions between the disinfectant (e.g. chlorine, chloramines, or ozone) and organic and inorganic compounds in the water, such as natural organic matter (NOM) and/or bromide. The two most abundant classes of DBPs are the THMs and HAAs (Krasner et al. 2006), which are also two of the most regulated DBP classes world-wide. The US Environmental Protection Agency (USEPA) regulates the sum of four THMs (THM4) at 80 µg L^{-1} and the sum of five HAAs (HAA5) at 60 µg L^{-1} based on running annual averages (US-EPA 2001). The Australian Drinking Water Guidelines level for THM4 in drinking water is 250 µg L^{-1}, and the levels for three chloroacetic acids, mono-, di- and tri-chloroacetic acid, are 150, 100 and 100 µg L^{-1}, respectively (NRMMC-NHMRC 2011).

Chlorination is the most widely used drinking water disinfection process, however, there is increasing interest in chloramination as an alternative disinfectant to chlorination (Seidel et al. 2005), particularly in North America, as water utilities work to comply with the ever more stringent water quality regulations. Chloramination has the advantage that it is known to produce much lower concentrations of regulated THMs and HAAs (Hua and Reckhow 2007). In addition, for bromide-containing waters, hypochlorous acid (HOCl) can oxidise bromide to hypobromous acid (HOBr), forming Br-DBPs. The formation of Br-DBPs is of concern to as they have been shown to be more harmful to human health than their chlorinated analogues (Bull et al. 2006; Richardson et al. 2007). Care must be taken, however, when considering risk trade-offs between various disinfection options because minimising regulated DBPs may inadvertently increase the formation of more toxic emerging DBPs (Krasner 2009).

As described in Section 1.5.2.2, the formation of the DBP class, the *N*-nitrosamines, is of concern to the water industry, since many of the *N*-nitrosamines have been reported to be carcinogenic, mutagenic, and/or teratogenic (O'Neill et al. 1984; Loeppky and Micheljda 1994). In their review on *N*-nitrosodimethylamine (NDMA) as a drinking water contaminant, Mitch et al. (2003a) summarise the occurrence of NDMA in drinking waters, particularly in chlorinated and chloraminated drinking

waters, starting with the first detections in Ontario (Canada) drinking waters in 1989 (Taguchi et al. 1994; Charrois et al. 2007), as well as in wells near rocket engine testing facilities (NDMA is reportedly a rocket fuel contaminant) in California, USA, in the early 2000s (DHS 2002; MacDonald 2002). A subsequent survey of California drinking waters showed the additional presence of NDMA at sites associated with aquifer recharge of chlorinated wastewater effluent, and some treated drinking waters from sources not associated with wastewater effluent or industrial impact, especially those sources using chloramination, but also some sites using chlorination, for disinfection (DHS 2002; Mitch et al. 2003a). NDMA occurs at low nanogram per litre concentrations in the latter drinking waters, and its recent detection in these drinking waters is reported to be largely a result of improved analytical techniques rather than changes in treatment practices (Mitch and Sedlak 2002).

More recently, analytical methods for the analysis of up to 9 *N*-nitrosamines in water samples have been developed (Charrois et al. 2004; Zhao et al. 2006; Van Buynder et al. 2009), allowing studies of their presence in various water matrices. The names and structures of these 9 *N*-nitrosamines are shown in Figure 1-1 in Section 1.5.2.2. Their tier classification, health value, and International Agency for Research on Cancer (IARC) classification are shown in Table 3-1.

As shown in Table 3-1, six of these *N*-nitrosamines have been classified as probable human carcinogens ('2B' group classification), and in addition, the US Environmental Protection Agency (US-EPA) has added six *N*-nitrosamines to the Unregulated Contaminant Monitoring Rule 2 (UCMR-2), representing 6 of the 26 compounds included in the UCMR-2 (US-EPA 2005). Several countries have adopted guideline values for the presence of NDMA and other *N*-nitrosamines in drinking water. The California Department of Public Health has established a notification level of 10 ng L^{-1} each for NDMA, *N*-nitrosodiethylamine (NDEA), and *N*-nitrosodi-n-propylamine (NDPA) (CDPH 2007), and the Ontario Ministry of the Environment (MOE) has issued a Maximum Acceptable Concentration of 9 ng L^{-1} for NDMA (MOE 2002). A health guideline value of 100 ng L^{-1} for NDMA has been included in the most recent iteration of the Australian Drinking Water Guidelines (NRMMC-NHMRC 2011).

Table 3 - 1: List of the nine *N*-nitrosamines with their tier classification, health value, and International Agency for Research on Cancer (IARC) classification (adapted from Van Buynder et al. 2009 and Linge et al. 2012)

Compounds	Tier[a]	Health value		IARC Group[c]
		µg/L	Source[b]	
N-Nitrosodimethylamine (NDMA)*	1	0.01	AGWR	2A
N-Nitrosoethylmethylamine (NEMA)*	2	0.002	IRIS	2B
N-Nitrosodiethylamine (NDEA)*	1	0.01	AGWR	2A
N-Nitrosodi-n-propylamine (NDPA)*	2	0.005	CalDPH	2B
N-Nitrosodi-n-butylamine (NDBA)*	2	0.006	IRIS	2B
N-Nitrosopiperidine (NPIP)	2	0.004	OEHHA	2B
N-Nitrosopyrrolidine (NPYR)*	2	0.02	IRIS	2B
N-Nitrosomorpholine (NMOR)	2	0.005	OEHHA	2B
N-Nitrosodiphenylamine (NDPhA)	2	7	IRIS	3

**chemical is on US-EPA's UCMR2 list*

[a] Tier value calculated by Van Buynder et al.(2009) using method described by Rodriguez et al. (2007): 1 = Regulated contaminants; 2 = Unregulated contaminants with toxicity information sufficient for health guideline derivation

[b] Source: AGWR = Australian Guidelines for Water Recycling; IRIS = US Environmental Protection Agency (US-EPA) Integrated Risk Information System; OEHHA = Office of Environmental Health Hazard Assessment (California); CalDPA = California Department of Public Health

[c] International Agency for Research on Cancer (IARC): Group 2A = Probable human carcinogen; 2B = Possible human carcinogen; 3 = Not classifiable as human carcinogen

Table 3-2 details several studies that analysed samples from drinking water treatment plants and distribution systems, either directly or after laboratory experiments. NDMA is the most studied and detected *N*-nitrosamine, and in drinking water is primarily found in waters treated with chloramine, where the nitrogen in chloramine is reportedly incorporated into the NDMA (Choi and Valentine 2002a). However, these studies also showed that, in a limited sample set, chlorination can potentially also produce *N*-nitrosamines.

Charrois et al. (2004) were the first to report *N*-nitrosamines other than NDMA in drinking water systems, when they analysed for eight *N*-nitrosamines in two locations (disinfection: chloramination and chlormination/UV) on two occasions in Alberta, Canada, and observed NDMA, NPYR and NMOR. After expanding their

Table 3 - 2: Summary of *N*-nitrosamines recently analysed and detected from samples taken from drinking water source waters, treatment plants, or distribution systems

Author	Disinfectants	NDMA	NEMA	NDEA	NDPA	NDBA	NPIP	NPYR	NMOR	NDPhA
						(ng L^{-1})				
Najm and Trussell (2001)	NH_2Cl	2 – 20	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Gerecke and Sedlak (2003)	NH_2Cl	7 – 59	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Charrois et al. (2004)*	NH_2Cl/UV	2 – 180	n.d.	n.d.	n.d.	n.d.	n.d.	2 – 4	1	n.a.
Zhao et al. (2006)*	NH_2Cl/UV	51 – 108	n.d.	n.d.	n.d.	n.d.	33 – 118	18 – 70	n.d.	0.6 – 1.9
Charrois et al. (2007)*	OCl^-, NH_2Cl	5 – 100	n.d.	n.d.	n.d.	n.d.	n.d.	3 – 4	2 – 3	n.a.
Planas et al (2008)*	OCl^-, O_3	1 – 10	n.d.	12 – 13	2.6	n.d	1.3	0.6 – 5	3 – 11	n.d.
Zhao et al. (2008)	NH_2Cl, OCl^-, OCl/UV, O_3, O_3/OCl^-	0 – 118	0 – 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	0 – 19	0 – 0.6
Goslan et al. (2009)*	NH_2Cl	0 – 26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.
Boyd et al. (2011)*	NH_2Cl, OCl^-, O_3/OCl^-	0 – 130	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0 – 2.2	0 – 1.8
Pozzi et al. (2011)*	O_3/OCl^-	n.d.	n.d.	8 - 30	8	11	n.d.	n.d.	83	n.d.

**Drinking water treatment plant or distribution samples without laboratory treatment*
n.a. = not analysed; n.d. = not detected

studies, Charrois et al. (2007) found six out of 20 distribution systems had at least one location where NDMA was detected. Of these six, one system used chlorination and five systems used chloramination for disinfection, either directly or by addition of chlorine to water with naturally elevated ammonia concentration. NMOR and NPYR were only detected in 2 chloraminated distribution systems (Charrois et al. 2007). Of the other studies summarised in Table 3-2, Planas et al (2008) analysed the concentrations of nine *N*-nitrosamines at a drinking water treatment plant on two occasions, with NDMA and NMOR detected in the influent waters, and NDMA, NDEA, NPYR and NMOR detected in the treated, chlorinated waters, in at least one sampling event. Zhao et al. (2008) investigated the formation of nine *N*-nitrosamines from seven natural source waters located in the US and Canada after eleven different disinfection treatments. Six of the seven waters contained NDMA prior to treatment and its concentration increased in five waters after disinfection with chloramine and in three waters after disinfection with chlorine. NEMA was detected (below the quantification limit) after chlorine disinfection of one water, and NDPhA was quantified after chloramination, and detected after chlorination (below the quantification limit), in another water sample. No *N*-nitrosamines were detected in any of the treated samples from the water with the lowest total organic carbon (TOC) concentration (2 mg L^{-1}) (Zhao et al. 2008). Boyd et al. (2011) investigated the formation of nine *N*-nitrosamines in 38 drinking water systems located in North America, with samples taken at drinking water treatment plants and within their distribution systems. NDMA was the most commonly detected *N*-nitrosamine, with the highest concentrations detected at one particular water treatment plant (chloramine disinfection) and its distribution system (29 and 130 ng L^{-1}, respectively). Two other *N*-nitrosamines were detected, with NMOR detected once at a water treatment plant (chloramine disinfection), and NDPhA detected 7 times within water treatment plants (chloramine, chlorine, and chlorine-ozone disinfection) and distribution systems (Boyd et al. 2011).

With drought and expanding populations resulting in scarcity of water in some regions of Australia, water of more marginal quality is increasingly being utilised for potable purposes. Reported studies of *N*-nitrosamines in Australian drinking water systems are extremely limited, with only NDMA having previously been analysed. Concentrations of NDMA during monthly monitoring in four South Australian

chloraminated systems over 3 years were found to be generally very low, but variable over seasons, with the maximum concentration being 54 ng L^{-1} (Newcombe et al. 2009). Further studies of the NDMA formation potential (FP) from chloramination of raw and treated water samples and a reservoir sample from sites in South Australia showed significant NDMA formation in all samples (up to 100, 150, and 300 ng L^{-1} in raw, filtered, and supernatant samples, respectively), with NDMAFP apparently increasing after treatment which included the amine-based coagulant, polydiallyldimethylammonium chloride (polyDADMAC), although there was no correlation between coagulant dose and NDMAFP (Morran et al. 2009a). During commissioning of a new pipeline in South Australia, elevated concentrations of NDMA were found to have resulted from leaching of NDMA from rubber rings used in the pipeline construction (Morran et al. 2009b).

3.1.1 Scope of Study

This Chapter describes a bench-scale study of the formation of eight *N*-nitrosamines from chlorination and chloramination of a Western Australian drinking water source water containing DOC (3.6 mg L^{-1}) and bromide (0.34 mg L^{-1}). There are no previous reports of studies of the formation of *N*-nitrosamines other than NDMA, nor of *N*-nitrosamine formation from chlorination, in Australian drinking waters. In addition to *N*-nitrosamines, four THMs (THM4), nine HAAs (HAA9) and five haloacetonitriles (HANs; HAN5) were also analysed to understand more fully the DBP formation potential of this source water.

3.2 Experimental

3.2.1 Water Sample

A raw water sample (75 L) was collected from a surface water source in the South-West of Western Australia, in February 2008. The catchment area is vegetated with relatively undisturbed native vegetation, and water flow into the reservoir is mostly from surface runoff. The sample was filtered through a pre-washed 0.45 µm membrane filter (Pall) into a stainless steel container (75 L), transported back to the laboratory and stored at 4ºC.

3.2.2 Solvents and Reagents

Laboratory water used throughout this Thesis was purified through a series of treatment steps in order to obtain water of sufficiently high purity. Pre-purified water (deionised water) was passed through an ELGA purification system, consisting of a 'primary' purification pack (LC147), UV chamber (LC118), a 'polishing' purification pack (LC147), Ultra-Microfilter (LC109), and finally a 0.2 µm point-of-use filter (LC134), which yielded high purity water with a resistivity of ≤ 18.2 mΩ and a total organic carbon concentration of ≤ 1 µg L^{-1}. This purified water will be referred to as 'laboratory water' throughout this Thesis.

All solvents and reagents used in this work were of analytical grade purity (AR grade ≥ 99% pure) or better, except for the aqueous sodium hypochlorite solution (12.5%, technical grade, Ajax Finechem). During the course of the Thesis research, the chlorine stock solution was found to be contaminated with a small amount of bromine. Chloramine (NH_2Cl) was prepared following the procedure of Cowman and Singer (1996), with a Cl_2 to N mass ratio of 4:1.

3.2.3 Measurement of Water Quality Parameters in Water Samples

3.2.3.1 Chlorine Equivalent Residual Measurements

Residual chlorine equivalent concentrations (free and total) were measured in duplicate using a Hach Pocket Colorimeter (HACH, Loveland, CO, USA), which is based on a colourmetric reaction of chlorine equivalents with *N*,*N*-diethyl-*p*-phenylenediamine (DPD).

3.2.3.2 Chloramine Residual Measurements

Residual chloramine concentrations were measured in duplicate using a Hach Pocket Colorimeter (HACH, Loveland, CO, USA), which is based on an Indophenol Method. The Hach Pocket Colorimeter measured monochloramine only.

3.2.3.3 UV_{254} Absorbance and Specific Ultraviolet Absorbance at 254 nm Measurements

The UV absorbance was determined using a HP 8452A Diode Array Spectrophotometer with a 5 cm quartz cell. Background measurements were performed using laboratory water. Specific ultraviolet absorbance at 254 nm

($SUVA_{254}$) was calculated as the ratio of the UV absorbance at 254 nm (m^{-1}) to the DOC concentration (mg C L^{-1}).

3.2.3.4 Dissolved Organic Carbon Analysis

The DOC concentration was determined by the UV/persulphate oxidation method, using a TOC-V WS Analyser (Shimadzu). All samples were filtered through a 0.45 µm membrane filter prior to analysis.

3.2.3.5 Nitrogen Measurements

The total nitrogen and total inorganic nitrogen were measured by a commercial laboratory (SGS Pty. Ltd.) according to test methods QPW-156 and QPW-145, respectively, which are based on Standard Methods APHA-4500. Dissolved organic nitrogen (DON) was determined by subtracting the total inorganic nitrogen from the total nitrogen. The limit of reporting for each nitrogen species was 50 µg L^{-1}.

3.2.3.6 Bromide Ion Measurements

Bromide was measured by a commercial laboratory (ChemCentre, Western Australia) according to the method iBRLOW1WA (bromide by ion chromatography (IC)), with a reporting limit of > 0.02 mg L^{-1}.

3.2.4 Chlorination and Chloramination of the Water Sample

Water samples (5 L) were buffered to pH 7 using a phosphate buffer, and subjected to chlorination, using a prepared concentrated stock solution of NaOCl (approximately 700 mg L^{-1} as Cl_2) to achieve a concentration of 0.10 mM (7 mg L^{-1}) as Cl_2, or chloramination solution to achieve a disinfectant concentration of 0.06 mM (3 mg L^{-1}) as NH_2Cl. A pH value of 7 was selected to enable direct comparison between the disinfection methods. After 24 hours, 72 hours, and 168 hours at 22°C, the disinfectant residual was quenched with an excess of aqueous sodium sulphite solution (APS Finechem) (21 mM) for THM and HAA analysis, and of ascorbic acid solution (Acros Organics) (21 mM) for HAN and *N*-nitrosamine analysis. At each sampling time, the concentrations of the residual equivalent chlorine or chloramine were also measured.

3.2.5 *N*-Nitrosamine Formation Potential from Chlorination and Chloramination of the Water Sample

Additional experiments at pH 7 were conducted to determine the *N*-nitrosamine formation potential of water samples. Following the procedure of Mitch and Sedlak (2004), sodium hypochlorite solution or chloramine solution was added in order to produce a chlorine concentration of 2 mM (142 mg L^{-1} as Cl_2), or a chloramine concentration of 2 mM (103 mg L^{-1} as preformed NH_2Cl). A 10-day reaction period was selected, after which time the residual equivalent chlor(am)ine was quenched using an aqueous ascorbic acid solution and the samples analysed for *N*-nitrosamines.

3.2.6 Disinfection By-Product Formation Measurements

3.2.6.1 Automated Headspace Solid-Phase Microextraction - Gas Chromatography-Mass Spectrometric (GC-MS) Analysis of Trihalomethanes

Four THMs (chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$) (THM4)) were analysed using the standard operating procedure for an existing method previously reported by Kristiana (2007). All samples were analysed in duplicate and blank samples were also analysed.

Briefly, an aliquot (10 µL) of an internal standard solution (50 mg L^{-1} 1,2-dibromopropane in methanol) was added directly into the sample (10 mL) contained in a 20 mL sample vial. Sodium sulphate (~1.67 g Na_2SO_4) (Ajax Finechem) was then added and the vial was capped. Automated extraction by headspace solid-phase microextraction (SPME) (using a divinyl/carboxen/polydimethylsiloxane fibre (Supelco®)) and analysis by GC-MS (Agilent Technologies Series II GC 6890N interfaced to an Agilent Technologies 5973N Mass Selective Detector) were carried out.

The limits of detection (LODs) were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004) by using the standard deviation of replicate analyses (n = 3) of standard solutions of 2, 50, and 100 µg L^{-1} concentration. The average LOD for $CHCl_3$ was 0.5 µg L^{-1} (4 nM), $CHBrCl_2$ was 1.0

µg L^{-1} (6 nM), while $CHBr_2Cl$ and $CHBr_3$ were 3.0 µg L^{-1} (14 and 12 nM, respectively).

3.2.6.2 Liquid-Liquid Extraction followed by GC-MS Analysis of Haloacetonitriles

Five haloacetonitriles (chloroacetonitrile (MCAN), bromoacetonitrile (MBAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), and trichloroacetonitrile (TCAN) (HAN5)) were analysed using a modified version of the US Environmental Protection Agency (US-EPA) Method 551.1 (Hodgeson and Cohen 1990). The modifications to the US-EPA Method 551.1 were: surrogate standard of 1,2-dibromopropane-d_6; internal standard of 1,1,2,2-tetrachloroethane-d_2; and the use of an Agilent Technologies Series II GC 6890N interfaced to a Agilent Technologies 5973N Mass Selective Detector. All samples were analysed in duplicate and blank samples were also analysed.

The LODs were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004) by using the standard deviation of replicate analyses (n = 3) of standard solutions of 5, 20, and 150 µg L^{-1} concentration. The average LOD for MCAN was 5.5 µg L^{-1}, MBAN was 8.5 µg L^{-1}, DCAN was 3.5 µg L^{-1}, DBAN was 9.5 µg L^{-1}, and TCAN was 4.0 µg L^{-1}.

3.2.6.3 Liquid-Liquid Extraction and Derivatisation followed by GC-MS Analysis of Haloacetic Acids

Nine haloacetic acids (chloroacetic acid (MCAA), bromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), tribromoacetic acid (TBAA) (HAA9)) were analysed by liquid-liquid extraction, with methyl *tert*-butyl ether (MtBE) as solvent, followed by derivatisation of the acids to their corresponding methyl esters using acidic methanol, and the methyl esters separated and detected by GC-MS. The standard operating procedure for the existing method (Kristiana et al. 2010), based on a modified version of the US-EPA Method 552.3 (Domino et al. 2003), was used. The modifications to the US-EPA Method 552.3 were: sample volume (50 mL); surrogate standard bromoacetic acid-d_6; internal standard 1,2-dibromopropane; sodium sulphate (19.5 g); volume of MtBE (3 mL); volume of acidic methanol (2.5

mL); and the use of an Agilent Technologies Series II GC 6890N interfaced to a Agilent Technologies 5973N Mass Selective Detector. All samples were analysed in duplicate and blank samples were also analysed.

The LODs were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004) by using the standard deviation of replicate analyses (n = 3) of standard solutions of 2, 25, and 10 µg L^{-1} concentration. The average LOD for MCAA was 8.5 µg L^{-1}, MBAA was 7.0 µg L^{-1}, DCAA was 10.0 µg L^{-1}, TCAA and DBCAA were 4.0 µg L^{-1}, BCAA, DBAA, and BDCAA were 3.0 µg L^{-1}, and TBAA was 6.0 µg L^{-1}.

3.2.6.4 Solid-Phase Extraction followed by GC-MS Analysis of N-*Nitrosamines*

Eight *N*-nitrosamines (Table 3-1; NDPhA was not analysed as it is thermally unstable and could decompose into diphenylamine in the GC injector (Eichelberger et al. 1983; Ho et al. 1990)) were extracted from the quenched samples by solid-phase extraction (SPE) and analysed by GC-MS, following the standard operating procedure for an existing method previously reported by Van Buynder et al. (2009), which was based on the method reported by Charrois et al. (2004). Due to sample volume restrictions, only one sample was analysed, and a blank sample was also analysed.

Briefly, an aliquot (7 µL) of a surrogate standard solution (2 ng L^{-1} deuterated *N*-nitrosamine standards (*N*-nitrosodimethyl-d6-amine (NDMA-d6), *N*-nitrosodiethyl-d10-amine (NDEA-d10), *N*-nitrosodi-n-propyl-d14-amine (NDPA-d14), *N*-nitroso-(n-butyl-d9)-amine (NDBA-d9), *N*-nitrosopiperidine-d10 (NPIP-d10), *N*-nitrosopyrolidine-d8 (NPYR-d8), *N*-nitrosomorpholine-d8 (NMOR-d8)) was added directly into the sample (1L). The *N*-nitrosamines were extracted using in-house SPE cartridges packed with LiChrolut® EN (Merck KGaA) and Carboxen™ 572 (Supelco) resins, followed by elution of the *N*-nitrosamines from the cartridge using dichloromethane (DCM), and concentration of the DCM extracts to approximately 300 µL. An aliquot (5 µL) of an internal standard solution (2 ng L^{-1} diphenylamine-d10) was added directly into the concentrated sample, which was then analysed by GC-MS in electron impact (EI) mode, using an Agilent Technologies Series II GC 6890N interfaced to a 5975 Inert Mass Selective Detector

equipped with a 30 m × 0.25 mm ID HP-INNOWAX (Agilent) column with a film thickness of 0.25 µm.

3.2.6.4.1 Limits of Detection and Relative Standard Uncertainties of N-*Nitrosamines*

The LODs were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004) by using the standard deviation of replicate analyses (n = 3) of standard solutions of 5, 10, and 20 ng L^{-1} concentration.

Relative standard uncertainties (Ellison et al. 2000) were calculated using an uncertainty budget that incorporated precision, calibration standard preparation, sample volume, and linear regression of the calibration curve. Data from this study were added to data previously obtained by Van Buynder et al. (2009) in order to broaden the data set and increase the LOD confidence. Sample homogeneity was considered a negligible source of uncertainty.

The average LODs and relative standard uncertainties are shown in Table 3-3. It should be noted that the LODs for NDBA, NPYR, and NMOR are above their respective health values (Table 3-1), therefore detection of these compounds in the sample would potentially be of health concern.

Table 3 - 3: Average LODs (ng L^{-1}) and the relative standard uncertainties (%) of the *N*-nitrosamines

***N*-Nitrosamine**	**Average LOD (ng L^{-1})**	**Relative standard uncertainty for 10 ng L^{-1} (%)**
NDMA	3	40
NEMA	1	35
NDEA	1	55
NDPA	1	30
NDBA	3	45
NPIP	1	45
NPYR	7	30
NMOR	3	30

3.3 Results and Discussion

3.3.1 The Source Water Sample

The water quality parameters of the surface water sample collected from the South-West of Western Australia (WA) are listed in Table 3-4. In comparison to other Western Australian drinking water sources where $SUVA_{254}$ values have been reported to range up to 6.87 L mg^{-1} m^{-1} (e.g. Warton et al. 2007), the $SUVA_{254}$ value of 2.6 L mg^{-1} m^{-1} is moderately low. Natural waters that contain mainly hydrophilic and low molecular weight NOM generally have $SUVA_{254}$ values less than 2.0, while waters containing hydrophobic and higher molecular weight NOM generally have SUVA values greater than 4.0 (Bekaroglu et al. 2010). It is therefore likely that the studied water source contains moderate amounts of high and low molecular weight NOM and aromatic carbon content.

Treatment of this water source for drinking purposes by the utility currently consists solely of disinfection with 3.5 – 4.5 mg L^{-1} chlorine, with the chlorine concentration varying, depending on the organic carbon concentration, prior to distribution. The monitoring of DBPs in the distribution system focuses on THMs. The disinfection of this water often results in distribution system total THM concentrations close to the Australian Drinking Water Guidelines value of 250 µg L^{-1}. Treatment options under consideration to improve the distributed water quality at this site include NOM removal technologies and the use of chloramination for disinfection. It is therefore important to more closely study the DBP formation, including the increasingly significant *N*-nitrosamines, from this source water under conditions of both chlorination and chloramination.

Table 3 - 4: Water quality parameters of the South-Western WA surface water sample used for disinfection by-product formation potential experiments

pH	7.2
DOC (mg L^{-1})	3.6
Bromide (mg L^{-1})	0.34
Total Nitrogen (mg L^{-1})	0.28
Total Inorganic Nitrogen (mg L^{-1})	0.09
Dissolved Organic Nitrogen (mg L^{-1})	0.19
UV_{254} (cm^{-1})	0.09
$SUVA_{254}$ (L mg^{-1} m^{-1})	2.6

3.3.2 Chlorination and Chloramination of the Source Water

To examine halogenated DBP (THM, HAA, and HAN) and *N*-nitrosamine formation from the source water under controlled laboratory conditions, sodium hypochlorite solution or chloramine solution were added to the water samples to obtain a target chlor(am)ine residual of 1 – 2 mg L^{-1} after a 7-day reaction period in order to simulate conditions applicable to Australian utilities. A time period of 7 days was chosen to be consistent with the Standard Methods procedure (Clesceri et al. 1998), and local water distribution times. During and after the reaction period, the residual oxidant in the samples was measured and quenched with either aqueous sodium sulphite solution (THM and HAA samples) or ascorbic acid solution (HAN and *N*-nitrosamine samples), and the resulting THM, HAA, HAN, and *N*-nitrosamine concentrations were determined.

3.3.2.1 Total Halogenated DBP Formation

The total halogenated DBP class concentrations observed after the 7-day reaction period, as well as the 7-day disinfectant demand, are presented in Table 3-5. Of the three halogenated DBP classes analysed, the THMs and HAAs were the two major groups observed, with only very low concentrations of HANs produced after chlorination and chloramination. The halogenated DBP concentrations from chloramination were significantly lower than those from chlorination, consistent with previous studies (e.g. Diehl et al. 2000; Bougeard et al. 2010). In this study, the observed THM and HAA concentrations were reduced by almost 97% and 94%, respectively, when chloramination was applied in comparison to chlorination, similar to reductions others have previously observed (e.g. Cowman and Singer 1996; Hua and Reckhow 2007).

After chlorination, the THM4 were in the greatest abundance, forming almost 4 times more (molar concentration) than the HAA9 (1.9 and 0.5 µM, respectively). Similar trends have been previously observed (e.g. Zhang et al. 2000), and Wu and colleagues (2003) accounted for this abundance by proposing that chlorine oxidises humic substances to a greater extent than chloramine, releasing more *m*-dihydroxybenzene moieties, which are THM precursors, and therefore forming proportionally more THMs than HAAs (Wu et al. 2003).

Table 3 - 5: Halogenated DBP formation after chlorination and chloramination (7 days)

	Concentration (µg L^{-1})			**Specific yield (µg mg^{-1} DOC)**			**Disinfectant demand* (mg L^{-1})**	**Specific disinfectant demand^ (mg mg^{-1} DOC)**	**Disinfectant/Br molar ratio**
	THM4	HAA9	HAN5	THM4	HAA9	HAN5			
Chlorination (as Cl_2)	300	170	7	83	28	0.014	5.6	1.56	23
Chloramine (as pre-formed NH_2Cl)	10	11	0.4	3	3	0.001	1.0	0.28	14

*the difference between the initial oxidant concentration and the residual after 7 days
^the disinfectant demand divided by the DOC concentration of the sample

The total THM4 concentration after the 7-day chlorination of this sample was 300 µg L^{-1}, exceeding the Australian Drinking Water Guidelines value of 250 µg L^{-1}, and the total HAA concentration was also elevated at just over 170 µg L^{-1}, however the Australian Drinking Water Guidelines values for MCAA, DCAA, and TCAA were not exceeded. The fairly high DBP values may be significant as the source water receives no pre-treatment for NOM removal prior to disinfection and, while the DBP concentrations are based on laboratory studies rather than distribution system concentrations, there remains the possibility for the distribution system to occasionally contain THM concentrations above the health guideline values. These results show the necessity for utilities to regularly test their distribution system water quality in order to remain in compliance with the water regulations, and to undertake source water quality monitoring in order to assess seasonal variations in water quality. Management of DBP formation can be achieved through additional water treatment processes, and methods for reduction of concentrations of already-formed DBPs in the distribution network can also be considered.

Specific yields of DBPs (the amount of DBP produced per mg of DOC) show the propensity of the type of NOM in the source water to form DBPs. The specific yields of the measured DBPs are also presented in Table 3-5. Kristiana (2007) previously studied samples taken after water treatment (including coagulation), prior to final disinfection, from several different local treatment plants where the DOC concentrations ranged between 1.5 – 5.1 mg L^{-1}, and found the 7-day specific yields of THMs and HAAs resulting from similar chlorination experiments ranged between 36 – 73 and 12 – 31 µg mg^{-1} DOC, respectively; and from similar chloramination experiments ranged between 9 – 13 and 3 – 6 µg mg^{-1} DOC, respectively. Although the source water used in the present study had no prior treatment, the THM and HAA formation after chlor(am)ination was similar compared to the treated water used by Kristiana (2007). In comparison, the source water in this study, which has had no prior treatment, appears to contain DOC with a higher potential to produce THMs from chlorination, but a lower potential to produce THMs from chloramination, while the HAA formation potential from both disinfectants is similar. This may be due to the presence of high molecular weight NOM in the sample, which would otherwise have been removed during water treatment. Coagulation/flocculation,

sedimentation and filtration are known to remove high molecular weight NOM, thereby reducing THM formation (Drikas et al. 2003).

The formation of the individual HAAs during the 7-day reaction period for chlorination and chloramination is shown in Figure 3-1 (no HAAs were detected prior to chlor(am)ination). HAA formation was observed to be significantly lower after chloramination than compared to chlorination. Only dihalogenated (X_2AAs) and trihalogenated (X_3AAs) species were detected after the 7-day reaction period for both chlorination and chloramination. The X_2AAs constituted the greatest mole fraction of the total HAA concentration (73% after chlorination; 90% after chloramination). Chloramination resulted in a change in the HAA speciation towards dihalo derivatives compared to chlorination, in which the formation of X_3AAs typically exceeds X_2AAs. During their survey of seven Scottish water treatment works, Goslan and colleagues (2009) reported that generally equal levels (based on mass concentrations) of X_2AAs and X_3AAs were formed in the chlorinated waters, while X_2AAs were always the major group found in chloraminated samples. Cowman and Singer (1996) observed the X_2AAs as the principal species formed after chloramination of aquatic humic substance extracts with a low Br^- concentration, however after chlorination, the X_3AAs were found to be the greatest mole fraction (61 – 67%), with X_2AA species making up 30 – 36% of the total HAAs. Diehl et al. (2000) reported that chloramines preferentially formed X_2AAs (> 80% of total HAAs), compared to chlorination. Karanfil et al. (2007) found evidence of a direct reaction between chloramine and NOM as the main pathway for HAA formation during chloramination, accounting for approximately 80% of the X_2AAs, with the remaining 20% of the X_2AAs resulting from reactions of NOM with HOCl which is present when free chlorine and ammonia are added to water to form chloramine *in situ*.

The predominant species formed after the 7-day reaction period were DCAA and BCAA for both chlorination and chloramination. Zhang and colleagues (2000) also observed DCAA to be the predominant species (25.2 µg L^{-1}) and TCAA to be much lower (0.33 µg L^{-1}) after chloramination of Suwannee river fulvic acid, and Bougeard et al. (2010) also found DCAA to be the predominant HAA formed after chloramination during their survey of eleven treatment works. It seems unusual,

however, that this source water did not produce considerable TCAA during chlorination, as both TCAA and DCAA are commonly reported as the predominant species formed during chlorination (e.g. Bougeard et al. 2010; Zhang et al. 2000; Goslan et al. 2009). It may be that the relatively high ratio of natural bromide in this water to chlor(am)ine added caused a shift from TCAA to the brominated HAAs, such as BCAA, due to the greater amount of bromide available to react with the disinfectant.

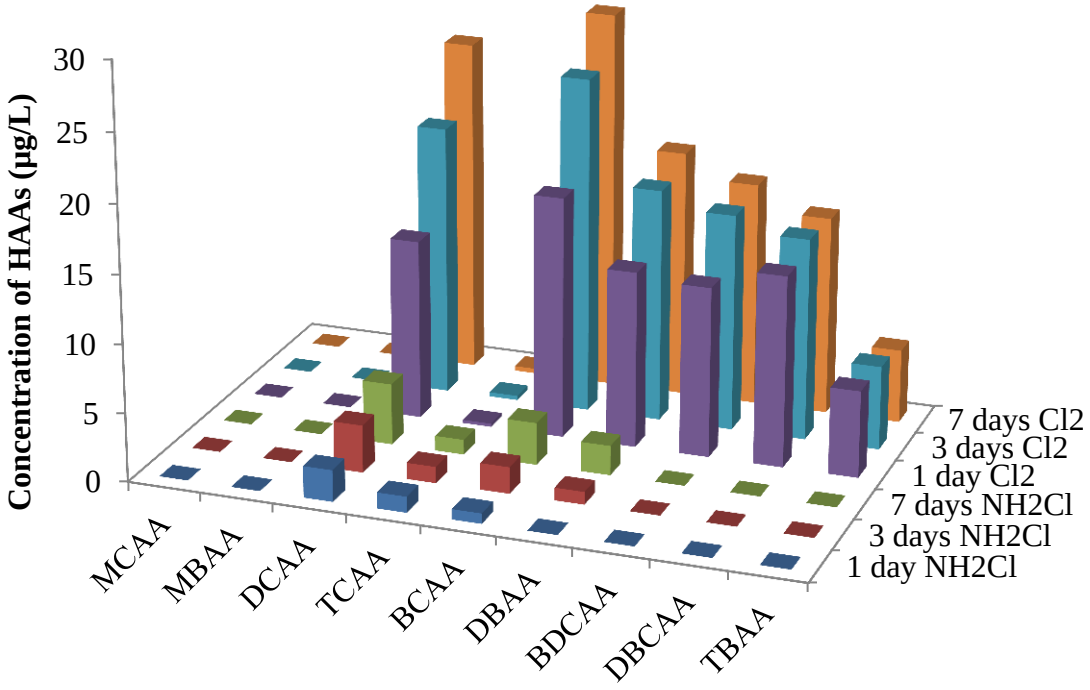


Figure 3 - 1: HAAs formed over 7 days after chloramination and chlorination of the sample

3.3.2.2 Bromine Incorporation into the Halogenated DBPs

The molar ratio of applied disinfectant to Br^- is shown in Table 3-5. The relative proportions of the individual THMs, based on molar concentrations, formed after the 7-day reaction period for chlorination and chloramination are shown in Figure 3-2. The relative proportions of brominated THMs were significantly higher with the use of chlorine rather than chloramine, and this has also been observed by others (e.g. Zhang et al. 2000; Hua and Reckhow 2007).

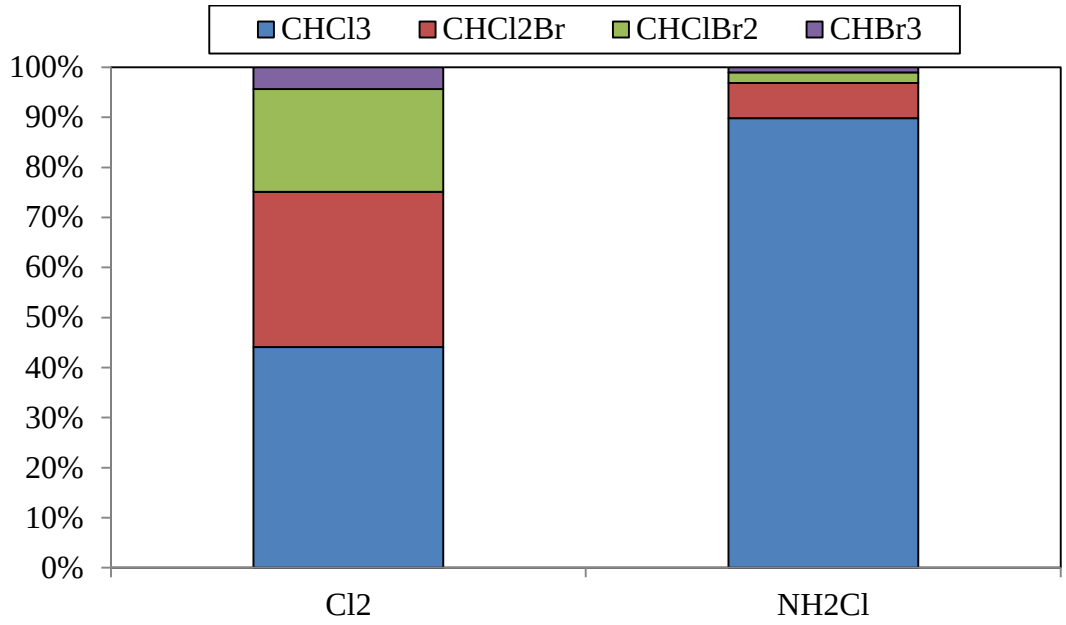


Figure 3 - 2: Relative proportions of the molar concentrations of THMs formed after 7 days from chlorination and chloramination experiments

The "Bromine Incorporation Factor" (BIF; Equation 1) is a parameter used to measure the extent of bromine substitution in a DBP class, as characterised by the ratio of moles of bromine to moles of total halogen incorporated into the various DBP classes (Boyer and Singer 2005).

$$\text{BIF (class)} = \frac{\Sigma \text{ (species molar conc)} \times \text{(species \# Br substituents)}}{\Sigma \text{ (species molar conc)} \times \text{(species \# halogen substituents)}} \quad (1)$$

As X_2AAs and X_3AAs have been found to have different precursors and be formed via different reaction mechanisms (Cowman and Singer 1996; Liang and Singer 2003), they can be considered as two separate classes of DBPs for the BIFs of the HAAs (Obolensky and Singer 2005).

The BIF values calculated for THM4, HAA9, X_2AAs, X_3AAs, and HAN5 after the 7-day chlor(am)ination experiments of the source water (containing 0.34 mg L^{-1} (4.3 µM) Br^-) are presented in Table 3-6. Only DBP species which were present above their detection limits were included.

Table 3 - 6: Bromine Incorporation Factors after 7-day chlor(am)ination of the source water

	THM4	HAA9	X_2AA	X_3AA	HAN5
chlorination	0.28	0.43	0.38	0.53	0.33
chloramination	0.05	0.27	0.31	-	-

Even though the disinfectant to bromine molar ratio (Table 3-5) was higher in the chlorination experiments, the BIFs from the chloramination experiment were lower than the BIFs from the chlorination experiment in all the DBP classes, i.e. the use of chloramine reduced the incorporation of bromine into the halogenated DBPs when compared to chlorination. This may be a result of low formation of HOBr from the intermediate bromamine in chloramination, or the lower stability of bromamines compared to chloramines (Diehl et al. 2000). These BIF results are consistent with trends reported previously (Cowman and Singer 1996; Qi et al. 2004; Kristiana 2007). The BIFs of the brominated X_2AAs showed the smallest difference between chlorination and chloramination. In addition, the proportion of X_2AA was lower than X_3AA after chlorination, while after chloramination the opposite was observed. Karanfil et al. (2007) found that it was the direct reaction between chloramine and NOM which was the main pathway for HAA formation during chloramination, observing approximately 80 % of X_2AAs resulted from reaction between chloramine and NOM at pH 6, while the remaining 20 % resulted from reaction of NOM with HOCl. The HAA9 BIF values are similar to those reported by Bougeard et al. (2010). In comparison to other Western Australian drinking water sources, the THM4 and HAA9 BIF values resulting from chlorination were similar to those observed in samples collected after NOM removal treatment (Kristiana 2007). Figure 3-3 shows the BIF (THMs) with respect to the BIF (X_2AAs) in the chlorination and chloramination experiments. The solid line in the figure represents the theoretical 1:1 line (x = y line), if bromine incorporation was the same for both DBP classes. Obolensky and Singer (2005) and Boyer and Singer (2005) showed that bromine incorporation was similar for THMs and X_2AAs. It can be seen that in both the chlorination and chloramination experiments, the data points were clustered above the x = y line, indicating there was slightly greater bromine substitution in X_2AAs than THMs. In comparison, Liang and Singer (2003) found the THMs from five treated (coagulation) waters had a higher molar proportion of brominated species

than the HAAs. The differences in bromine incorporation between the sample in the current study and the waters studied by Liang and Singer (2003) are likely to be a result of differences in relative amounts of hydrophobic and hydrophilic NOM in the different water types, as Liang and Singer (2003) reported that bromine is more reactive towards aliphatic precursors and the hydrophilic NOM fraction, rather than the hydrophobic fraction and aromatic precursors.

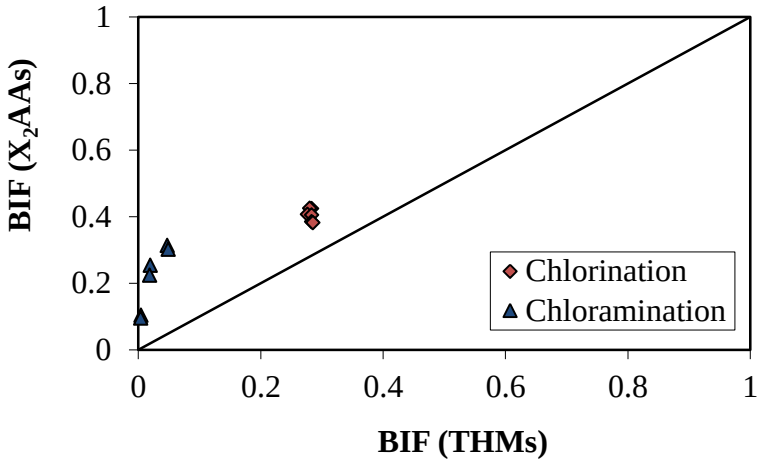


Figure 3 - 3: BIF (THMs) vs. BIF (X_2AAs) in the chlorinated and chloraminated water samples for all contact times, as molar concentrations (µM)

3.3.2.3 *N*-Nitrosamine Formation

Two of the eight *N*-nitrosamines (NDMA and NDEA) were detected at trace concentrations after the 7-day disinfection with either chlorine (9 and 4 ng L^{-1}, respectively) or chloramine (5 and 2 ng L^{-1}, respectively). The other six *N*-nitrosamines (NEMA, NDPA, NDBA, NPIP, NPYR, NMOR) were below their respective limit of detection. From the South-West WA source water, the detected *N*-nitrosamines appeared to reach their maximum formation relatively quickly, after approximately 24 hours. These compounds did not exhibit any overall degradation over the remaining 6 days of the experimental period (Figure 3-4).

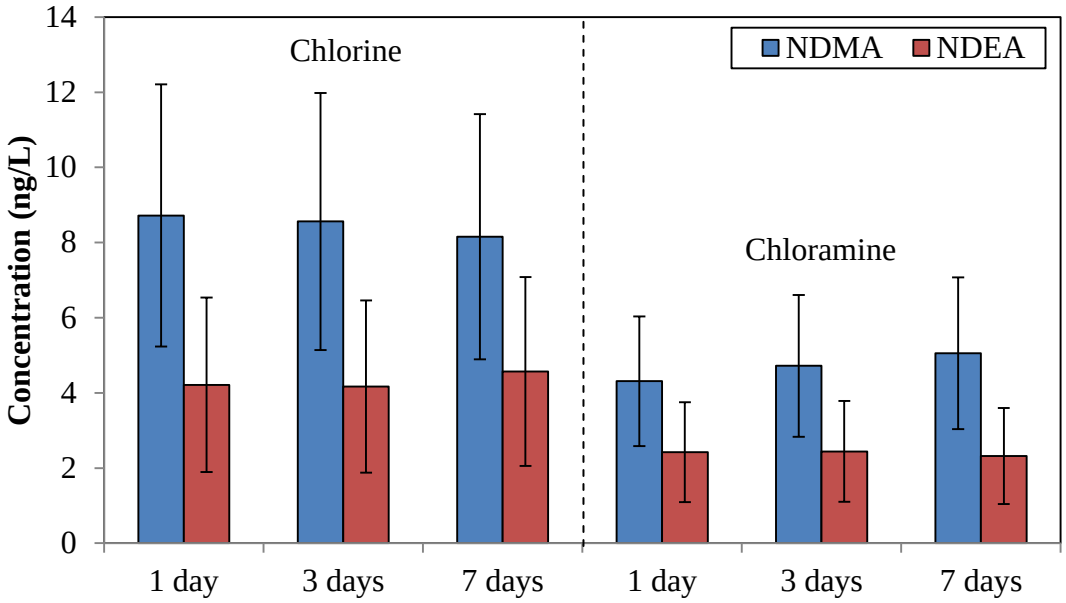


Figure 3 - 4: *N*-nitrosamines formed over 7 days after chlorination and chloramination of the sample

In these chlorination and chloramination experiments, neither the Australian Drinking Water Guidelines health value of 100 ng L^{-1} for NDMA, nor the California notification value of 10 ng L^{-1}, was exceeded. Although it was found that NDMA formed during the 7-day chlorination experiment was detected up to 9 ng L^{-1}, the chlorine dose used in the field (3.5 – 4.5 mg L^{-1}) is lower than the chlorine dose (7 mg L^{-1}) used in these experiments, so any concentrations of NDMA formed in the distribution system would be expected to be lower than those observed in these experiments.

Interestingly, while chlorination produced higher concentrations of NDMA in the current study than chloramination, in previous studies chloramination has been more commonly found to produce NDMA than chlorination, although NDMA production from chlorination has been reported (see Table 3-2). The detection of NDEA from chlor(am)ination of the South-West WA source water is of significant interest since there has been only one previous report of the formation of NDEA in drinking water systems. Planas et al. (2008) reported that NDEA formed at a concentration of 12.9 ng L^{-1} after chlorination in a drinking water treatment plant (1 – 1.2 mg L^{-1} free chlorine residual, sample taken at plant outlet), and at a concentration of 4.1 ng L^{-1}

after 24-hour laboratory chlorination (5 mg L^{-1} free chlorine) of a surface water which supplied a different drinking water treatment plant.

The formation of *N*-nitrosamines during chlorination and chloramination is complex, and several possible mechanisms have been proposed for NDMA formation. Under chlorination conditions, natural ammonia and natural amines (primary, secondary, and tertiary amines) in source waters, or amine-based coagulants used in the water treatment process, have been proposed as nitrogenous precursors for *N*-nitrosamine formation (Wilczak et al. 2003; Mitch et al. 2003a; Shah and Mitch 2012). Choi and Valentine (2003) noted that formation also occurs during chlorination of nitrite-containing waters (not relevant to the current study), where the production of dinitrogen tetraoxide can nitrosate or nitrate amines. Under chloramination conditions (or chlorination in the presence of natural ammonia resulting in chloramine formation), Schreiber and Mitch (2006a) proposed a reaction pathway where chlorinated 1,1-dimethylhydrazine (UDMH) is formed from the reaction between secondary amines and dichloramine, a product of the disproportionation of chloramine. The UDMH-Cl is then oxidised by dissolved oxygen to form the *N*-nitrosamine. Schreiber and Mitch (2007) added to this by suggesting another pathway which occurs during breakpoint chlorination (Cl_2:NH_3 ratios > 1.5) involving a series of free radical reactions. Reactive breakpoint chlorination intermediates (the identities of which are unclear) were postulated to be involved in the nitrosation of dimethylamine (Schreiber and Mitch 2007).

In addition, bromide has been reported to increase NDMA formation by producing bromine or bromamine (NH_2Br), which can then react with the organic matter (Mitch et al. 2003a; Shah et al. 2012). Given the identification of *N*-nitrosamine species other than NDMA, it is likely that there are a variety of precursors and conditions which may lead to *N*-nitrosamine formation. In the current experiments, it appears that there may have been different *N*-nitrosamine precursors for chlorination and chloramination reactions, resulting in differences in the formation of the different *N*-nitrosamines after oxidant addition.

The DOC/DON ratio of the sample water was 19 mg of DOC per mg of DON, which is average when compared to values obtained by Lee et al. (2007c), who suggested

that DON could be a surrogate parameter for the determination of NDMA formation potentials. However, there has been mixed success for DON being used to predict NDMA formation. Chen and Westerhoff (2010) reported that the inclusion of DON in their NDMA prediction model using bulk parameters (DOC, UV_{254}, and bromide) did not result in successful formation predictions from potable or surface waters, while Xu et al. (2011) found a strong linear regression correlation between NDMA formation potential and DON using a river water supplying a drinking water treatment plant, as well as samples taken throughout the treatment process at the plant. While it is likely DON concentrations have an impact on *N*-nitrosamine formation, it is difficult to use the parameter on its own to compare different waters.

Interestingly, the formation of the detected *N*-nitrosamines did not increase significantly over the 7-day reaction period (Figure 3-4), which is different to results which other researchers have obtained on various drinking water sources. When examining the occurrence of eight *N*-nitrosamines in Alberta public drinking water distribution systems, Charrois et al. (2007) found that *N*-nitrosamines can continue to form in the distribution system, as there were increased levels in the distribution system compared at the treatment plants. Zhao et al. (2006) also found the concentration of the detected *N*-nitrosamines (NDMA, NPYR, NPIP, and NDPhA) generally increased with increasing distance from a water treatment plant. Zhao et al. (2006) proposed that the residual disinfectant continued to react with the organic matter in the water until a maximum of *N*-nitrosamine concentration occurred where both formation and decomposition were balanced. It is therefore important to assess the total *N*-nitrosamine formation potential of the water, to determine whether continued exposure to the disinfectant may result in increased *N*-nitrosamine formation.

3.3.3 Total *N*-Nitrosamine Formation Potential from Chlorination and Chloramination of the Source Water

To examine the formation potential of *N*-nitrosamines from this drinking water source, high concentrations of sodium hypochlorite or pre-formed chloramine were added to the water sample to produce overall 2 mM chlorine (142 mg L^{-1} as free Cl_2) and chloramine (103 mg L^{-1}) concentrations. The 10-day formation of the only two detected *N*-nitrosamines is shown in Figure 3-5. Interestingly, the *N*-nitrosamine

concentrations formed after the high chlorination dose did not increase significantly over those formed after 7 days in the more conventional-dose experiment, while the high chloramination dose substantially increased the two *N*-nitrosamine concentrations compared to the conventional-dose experiment.

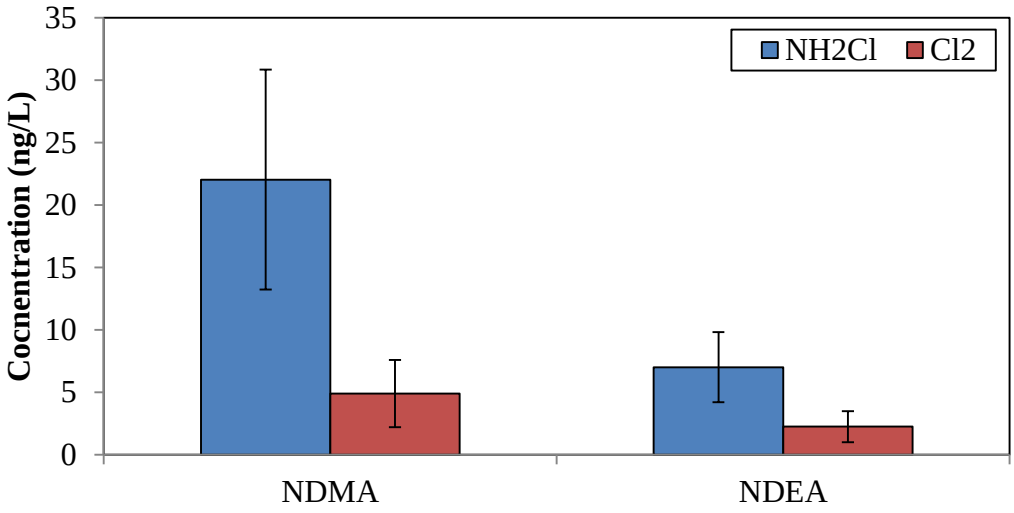


Figure 3 - 5: *N*-Nitrosamine formation potential after 10 days during the high dose (2 mM) chlorination and chloramination experiments

Other researchers have performed high-dose experiments in order to determine the total NDMA formation potential in drinking or source waters (Mitch et al. 2003b; Chen and Valentine 2006; Chen and Valentine 2007; Chen and Westerhoff 2010), however, to our knowledge, this is the first study to include the analysis of other *N*-nitrosamines and to assess the formation potential from chlorination. Chen and Westerhoff (2010) investigated the formation potential of NDMA from 168 samples of different types of source waters. Chloramination, where chlorine was added to the sample water at 3 x DOC concentration (on a weight basis) and ammonia was spiked when required at a Cl_2/N ratio of < 4:1, was used. The drinking water treatment plant, groundwater, and river samples had average NDMA formation potentials of 33, 16, and 340 ng L^{-1}, respectively (Chen and Westerhoff 2010). Chen and Valentine (2006) found the 7-day NDMA formation potential after 1 mM chloramine addition to an Iowa River sample was 112 ng/L. In comparison to these studies, the Western Australian surface water NDMA formation potential from chloramination was significantly lower than NDMA previously observed in river systems. These

differences are likely due to the quality of the water source (the Iowa River is heavily impacted by agricultural practices (Chen and Valentine 2006) compared to the pristine water used in the current study). However, the total NDMA formation potential using a high initial concentration of disinfectant in order to exhaust the NDMA precursors was similar to the average values observed from the 9 drinking water treatment plants and 10 groundwaters studied by Chen and Westerhoff (2010).

The Australian Drinking Water Guidelines value of 100 ng L^{-1} for NDMA was not exceeded during the total formation potential experiments. While the California Department of Public Health NDMA notification level (10 ng L^{-1}) was exceeded in the chloramination experiment, it should be noted that such a high dose of chloramine would not be used in practice.

3.4 Conclusions

The total THM concentration after 7-day laboratory chlorination of the source water was found to exceed the Australian Drinking Water Guidelines 250 µg L^{-1} value, which demonstrates the importance of regular DBP monitoring in the distribution system in order to ensure compliance with drinking water regulations. As the source water is not treated to remove NOM prior to disinfection, it is possible that THM concentrations over the guideline value may occasionally form within the distribution system. Further treatment prior to disinfection, or lower doses of disinfectant, without compromising disinfection processes, need to be considered for this source water in order to lower DBP formation on a precautionary basis. Methods for reduction on the concentration of already-formed THMs in the distribution network could also be useful. Regular source monitoring in order to understand how DBP formation varies over the course of the year is also recommended for improved management of DBP formation.

Low concentrations of the emerging DBP class, *N*-nitrosamines, were formed from chlorination of this source water. Of the eight *N*-nitrosamines analysed, NDMA and NDEA were detected after both chlorination and chloramination. This is the first report of the formation of *N*-nitrosamines other than NDMA, as well as the formation of *N*-nitrosamines from chlorination, in Australian drinking water systems. The total formation potentials of NDMA in the source water from both chlorination and

chloramination were determined, as well as the first reported formation potential values for the other seven analysed *N*-nitrosamines, with a detectable value for NDEA observed. NDMA and NDEA formation significantly increased with the higher chloramine dose, while the *N*-nitrosamines did not increase significantly with the higher chlorine dose.

Chapter 4

INVESTIGATION INTO THE OPTION OF OZONATION TREATMENT AT THE JANDAKOT GROUNDWATER TREATMENT PLANT, WESTERN AUSTRALIA

4.1 Introduction

The Jandakot Groundwater Treatment Plant (GWTP) treats groundwater from the Jandakot Mound, an important source water for Water Corporation's Perth Integrated Water Supply System (IWSS). However, this source water contains elevated concentrations of dissolved organic carbon (DOC) (5 – 25 mg L^{-1} (WCWA 2009)) and relatively high bromide concentrations (potentially > 1 mg L^{-1}), leading to the need for extensive treatment prior to utilisation. The present water treatment process at the Jandakot GWTP consists of pre-chlorination followed by coagulation/clarification and filtration, with final disinfection using chlorine. However, this process does not produce sufficient DOC removal, and the relatively high concentration of residual DOC (1 – 5 mg L^{-1} (WCWA 2009)) can result in disinfection by-product (DBP) formation which is often in excess of guideline values. The Australian Drinking Water Guidelines set the maximum level of total THMs (THM4) in disinfected water to be 250 µg L^{-1} (NRMMC-NHMRC 2011). As a result, the Jandakot GWTP product water needs to be blended with higher quality water, such as desalinated water, in the IWSS in order to reduce the concentration of DBPs in water distributed to customers.

Ozonation in combination with biological activated carbon (BAC), a process which is standard practice for drinking water treatment in many countries, particularly in Europe, can result in a significant reduction of DOC concentration. Ozone (O_3) reacts with DOC to form smaller molecules (often summarised under the term assimilable organic carbon (AOC) or biologically degradable organic carbon (BDOC)) that can be mineralised by a microbial consortium on a biological filter such as BAC (Hammes et al. 2006) and results in an overall reduction of DOC concentration. Ozone reacts specifically with certain chemical functional groups within the natural organic matter (NOM), such as double bonds, activated aromatic systems, and non-protonated amines (Hoigne and Bader 1983a; Hoigne and Bader 1983b; von Gunten 2003b), which can break larger molecules into smaller molecules and also lead to a reduction in the formation of halogenated DBPs upon post-chlorination because these functional groups have been removed or deactivated to reaction with halogen.

The study described in Chapters 4 – 6 was designed to investigate the option of introducing an ozonation treatment process into the Jandakot GWTP with a key goal being to reduce THM formation in the product water, while minimising the formation of bromate. The chemistry of the ozonation of drinking water can be extremely complex due to the large number of competing or simultaneous reactions that may occur (von Gunten 2003a; von Gunten 2003b). Jandakot raw water contains bromide at concentrations which are high (potentially >1 mg L^{-1}) compared to typical waters (< 0.65 mg L^{-1} (von Gunten 2003a)) treated with ozone, and a high concentration of bromide may cause problems in an ozonation process due to formation of the probable human carcinogen bromate (US-EPA 2006). Despite the many beneficial effects of ozonation, bromate formation is often the limiting factor for its application. The formation of bromate from bromide ion involves a complicated reaction mechanism of parallel reactions with ozone and hydroxyl radicals (•OH) (von Gunten and Hoigne 1994). Bromate formation is influenced by the presence of ammonia, organic amines, and chloramine (von Gunten 2003a; Buffle and von Gunten 2006), the former two species being present in appreciable concentrations in Jandakot raw water. The presence of chloramines may depend on whether pre-chlorination is employed in the process, adding to the complexity of the problem of bromate formation. The study described in Chapters 4 – 6 therefore focused solely on the complex chemistry of the ozonation step alone, and a series of well-controlled laboratory tests were conducted to determine the influence of a number of factors on the reactions of ozone with NOM, as well as with naturally occurring bromide and iodide. These factors included the influence of the raw water matrix, chlorination prior to the ozonation step (to model prechlorination in the treatment plant), pH, and alkalinity.

4.1.1 Ozone in Drinking Water Treatment

In aqueous solution, oxidation by ozone follows two reaction pathways: direct oxidation by ozone, or oxidation by the hydroxyl radicals (•OH) which are formed as secondary oxidants from ozone decomposition (von Gunten 2003b). Disinfection occurs predominantly through the action of ozone itself, while oxidation can occur through reactions with both ozone and •OH radicals (von Gunten 2003b).

The chemical nature of NOM strongly controls its reactivity with ozone, and affects not only the ozone consumption in ozonated waters, but also the competition for •OH. It has been shown that rate constants for the reaction of model organic compounds with ozone and •OH are dependent on the chemical structures and functional groups of the compounds (Hoigne and Bader 1983a; Hoigne and Bader 1983b).

Ozone is very selective in its reactions, and preferentially reacts as an electrophile, oxidising electron-rich moieties such as carbon-carbon double bonds, activated aromatic moieties, and amines (Hoigne and Bader 1983a; Hoigne and Bader 1983b; von Gunten 2003b). It has been found that, in general, electron-donating groups on the organic compounds enhance the oxidation rate by ozone, while electron-withdrawing groups reduce reaction rates (von Gunten 2003b), consistent with the electrophilic nature of ozone. The kinetics of the direct oxidation by ozone depend on the presence of electron-rich reactive moieties in organic molecules, such that olefins, activated aromatic systems, and deprotonated amines react fast, whereas many other moieties have intermediate to low reactivity with ozone. The selectivity of ozone is reflected by the range of second-order rate constants over 10 orders of magnitude, between $< 0.1 - 7 \times 10^9$ $M^{-1}s^{-1}$, for ozone oxidation of organic and inorganic compounds (von Gunten (2003a) and references therein). More than 500 rate constants have been measured for the reactions of ozone with numerous organic and inorganic species (Hoigne and Bader 1983a; Hoigne and Bader 1983b; Hoigne et al. 1985; Neta et al. 1988; Yao and Haag 1991). In comparison, •OH radicals have low selectivity and readily react with the water matrix and ozone, resulting in very low steady-state concentrations of •OH, typically below 10^{-12} M during ozonation (von Gunten 2003b). Several researchers have found that the $SUVA_{254}$ correlates well with ozone consumption rate parameters (Westerhoff et al. 1999; Elovitz et al. 2000a), implying that organic π-electrons strongly and selectively influence oxidative reactivity (Westerhoff et al. 1999). In contrast, •OH have been found to react rapidly and relatively unselectively with model organic compounds, though it has been reported that most carbon-carbon double and triple bonds react more quickly than carbon-hydrogen bonds (Buxton et al. 1988; Haag and Yao 1992). Several thousand rate constants have been measured for the reactions of •OH with organic and inorganic species (Buxton et al. 1988; Haag and Yao 1992).

In the first part of two reviews on the ozonation of drinking water, von Gunten (2003a) , describes the two ways in which NOM can affect the stability of ozone. The first is through a direct reaction of NOM with ozone. Here, depending on the type of NOM, the NOM can either be oxidised into new NOM by-products ($NOM1_{ox}$) (Equations 1), or it can form superoxide radicals ($\bullet HO_2/\bullet O_2^-/\bullet O_3^-$) (Equation 2).

$$O_3 + NOM1 \rightarrow NOM1_{ox} \quad (1)$$

$$O_3 + NOM2 \rightarrow \bullet NOM2^+ + \bullet O_3^- \quad (2)$$

Once these superoxide radicals are produced, they can react further with ozone to form more •OH (as discussed in Section 2.2.1). Therefore, the presence of NOM may alter the ozone reaction, increasing the ratio of •OH to ozone available in the system. The second mode in which NOM can affect the stability of ozone is an indirect reaction through the scavenging of •OH, where there is a chain reaction which begins with initiation, leading to an accelerated decrease in ozone. In this instance, there is the potential for the formation of carbon centred radicals (•NOM3), which can then react with oxygen to form superoxide radicals (Equations 3 – 4):

$$\bullet OH + NOM3 \rightarrow \bullet NOM3 + [H_2O \text{ or } OH^-] \quad (3)$$

$$\bullet NOM3 + O_2 \rightarrow NOM3^+ + \bullet O_2^- \quad (4)$$

The decrease in ozone resulting from the scavenging of •OH can be terminated by inhibitors, e.g. functional groups within NOM (NOM4), which do not liberate superoxide after reaction with •OH (Equations 5 – 6):

$$\bullet OH + NOM4 \rightarrow \bullet NOM4 + H_2O \quad (5)$$

$$\bullet NOM4 \rightarrow \text{products} \quad (6)$$

Carbonate and bicarbonate are also chain reaction inhibitors, and therefore alkalinity greatly affects the stability of ozone in natural waters (Equations 7 – 8):

$$CO_3^{2-} + \bullet OH \rightarrow \bullet CO_3^- + OH^- \quad (7)$$

$$HCO_3^- + \bullet OH \rightarrow \bullet CO_3^- + H_2O \quad (8)$$

The application of ozone in water treatment processes requires a balance between disinfection to enable pathogen inactivation, and control of DBP formation. In order to optimise water treatment with ozone, the ozone and •OH exposures, which are the oxidant concentrations integrated over time ($\int[\bullet OH]dt$ and $\int[O_3]dt$), need to be assessed for each water type. Elovitz and von Gunten (1999) developed the R_{ct} concept, which is a way of indirectly measuring •OH concentrations during the ozonation of waters. R_{ct} represents the ratio of •OH exposure and ozone exposure:

$$R_{ct} = \frac{\int[\bullet OH]dt}{\int[O_3]dt} \quad (9)$$

Briefly, an ozone-resistant probe compound for •OH (*para*-chlorobenzoic acid (pCBA)) is added to the water sample at very low concentrations, so as to ensure it does not significantly contribute to the overall scavenging of •OH, prior to ozonation in order to indirectly measure the transient •OH concentration. The probe compound reacts rapidly with •OH, but has low reactivity towards ozone, therefore:

$$\ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -k_{\bullet OH/pCBA}\int[\bullet OH]dt \quad (10)$$

The ozone concentration and the decrease of the pCBA concentration are then measured simultaneously. This allows the R_{ct} to be calculated via the slope of the logarithmic decrease in pCBA plotted against the ozone exposure (substitution of Equation 9 into Equation 10):

$$\ln\frac{[pCBA]}{([pCBA]_0)} = -R_{ct} \times k_{\bullet OH.pCBA} \times \int O_3 dt \quad (11)$$

where $k_{\circ OH.pCBA}$ = 5 x 10^9 M^{-1} s^{-1} (Neta and Dorfman 1968).

For a given set of water quality parameters, often the R_{ct} during the initial phase of ozonation is not constant, while it is constant in the second phase (Elovitz et al. 2000b). Under standard ozonation conditions and ozone-based advanced oxidation processes, an R_{ct} between 10^{-7} – 10^{-9} can be expected (Elovitz et al. 2000a). An increase in pH, temperature, or natural organic matter (NOM) concentration, or a

decrease in bicarbonate concentration, generally result in an increase in the R_{ct} value (Elovitz et al. 2000b).

4.1.2 The Jandakot Groundwater Treatment Plant

The Jandakot GWTP is located to the south of the city of Perth, and draws groundwater from the Jandakot Mound which consists of three aquifers: a shallow sand surficial aquifer; and the deeper confined Leederville and Yarragadee aquifers. The Jandakot Mound covers an area of approximately 540 km^2, reaching from the Swan River in the north to the Serpentine river in the south, and extending from the Indian Ocean in the west to the Darling Scarp and Southern River in the east (Davidson 1995; WCWA 2010). The Water Corporation of Western Australia (WCWA) began development of the Jandakot groundwater scheme in 1979, and the second stage of its development was achieved in 1993 (WCWA 2010). Plant production can vary between 19 and 47 ML per day, depending on demand, and the bore combination may change frequently during water production. As a result of the altering characteristics of the groundwater blends, treatment of Jandakot raw water is extremely challenging.

A plan of the Jandakot bore field is shown in Figure 4-1. Two confined Leederville aquifer bores (indicated in green) are up to 500 m deep, while the remaining 26 bores draw water from the surficial aquifer (indicated in red), and are up to 40 m deep. In the 2010/2011 year, 8.1 GL of water was abstracted from the Leederville aquifer, and 5.1 GL from the surficial aquifer; a total of 13.2 GL from the Jandakot system. The Yarragadee aquifer bore (indicated in blue) is over 700m deep, and the water from this bore is not supplied into the Jandakot GWTP but instead is blended with water supplied into the Melville reservoir due to the elevated temperature and salinity of the Yarragadee water. At present, no Yarragadee aquifer bores are connected to the Jandakot GWTP, however there is potential for expansion of the plant to include treatment of a Yarragadee bore (WCWA 2010).

Groundwater from the Jandakot Mound requires treatment to comply with Australian drinking water guidelines. The surficial aquifer contains ferrous ion (< 1 to > 50 mg L^{-1}), high DOC (up to 50 mg L^{-1}), colour (humic material), and turbidity (colloidal particles) (Davidson 1995). The salinity, measured as total dissolved solids

(TDS), in the deeper Leederville aquifer production bores ranges from 180 to 2500 mg L^{-1}, while the iron concentrations range from 0.42 to 18 mg L^{-1} (Davidson 1995). If connected to the Jandakot GWTP system, the Yarragadee water would add further complexity to the treatment as the salinity of this groundwater varies from approximately 140 to > 10 000 mg L^{-1} TDS and is rich in sodium chloride (Davidson 1995). The concentrations of water treatment chemicals used during drinking water treatment at the Jandakot GWTP depend greatly on plant production and which bores are online at a particular time. Figure 4-2 shows an overview schematic of the treatment system at the GWTP. There is an initial chlorination step (up to 8 mg L^{-1} Cl_2), followed by coagulation with aluminium sulphate (approximately 125 mg L^{-1}) which results in a slight decrease in pH. Polyelectrolyte is added, and the water then passes to the clarifier where floc is allowed to settle. The clarified water then flows on to one of three filters. All three filters are comprised of layers of blue metal, beach pebbles, and sand, however Filters 1 and 2 also contain anthracite, while Filter 3 contains granular activated carbon (GAC). After filtration, the water passes to a clearwater tank, where it is chlorinated for disinfection (average Cl_2 dose: 6.3 mg L^{-1}) prior to being pumped to Lake Thompson Reservoir.

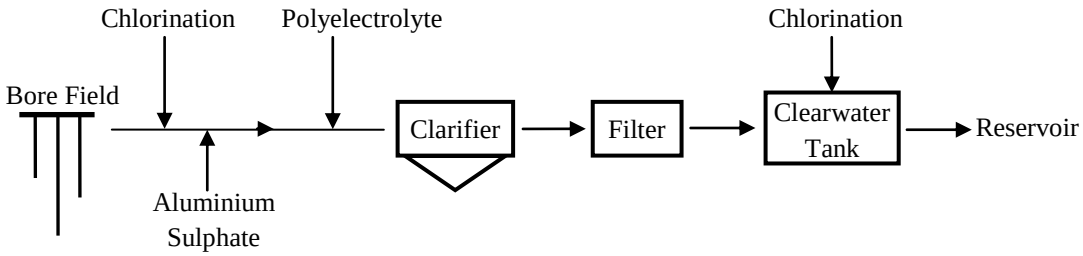


Figure 4 - 1: Overview schematic of the Jandakot Groundwater Treatment Plant

It is not only the continual variation in characteristics of the groundwater blends which are used as raw water for the plant which makes treatment problematic, but the general characteristics of the water itself. Average, minimum and maximum values of several water quality parameters at several stages of the water treatment process are listed in Table 4-1. The raw water contains very high concentrations of bromide (0.42 – 1.02 mg L^{-1}), which is challenging for chlorination processes (due to the

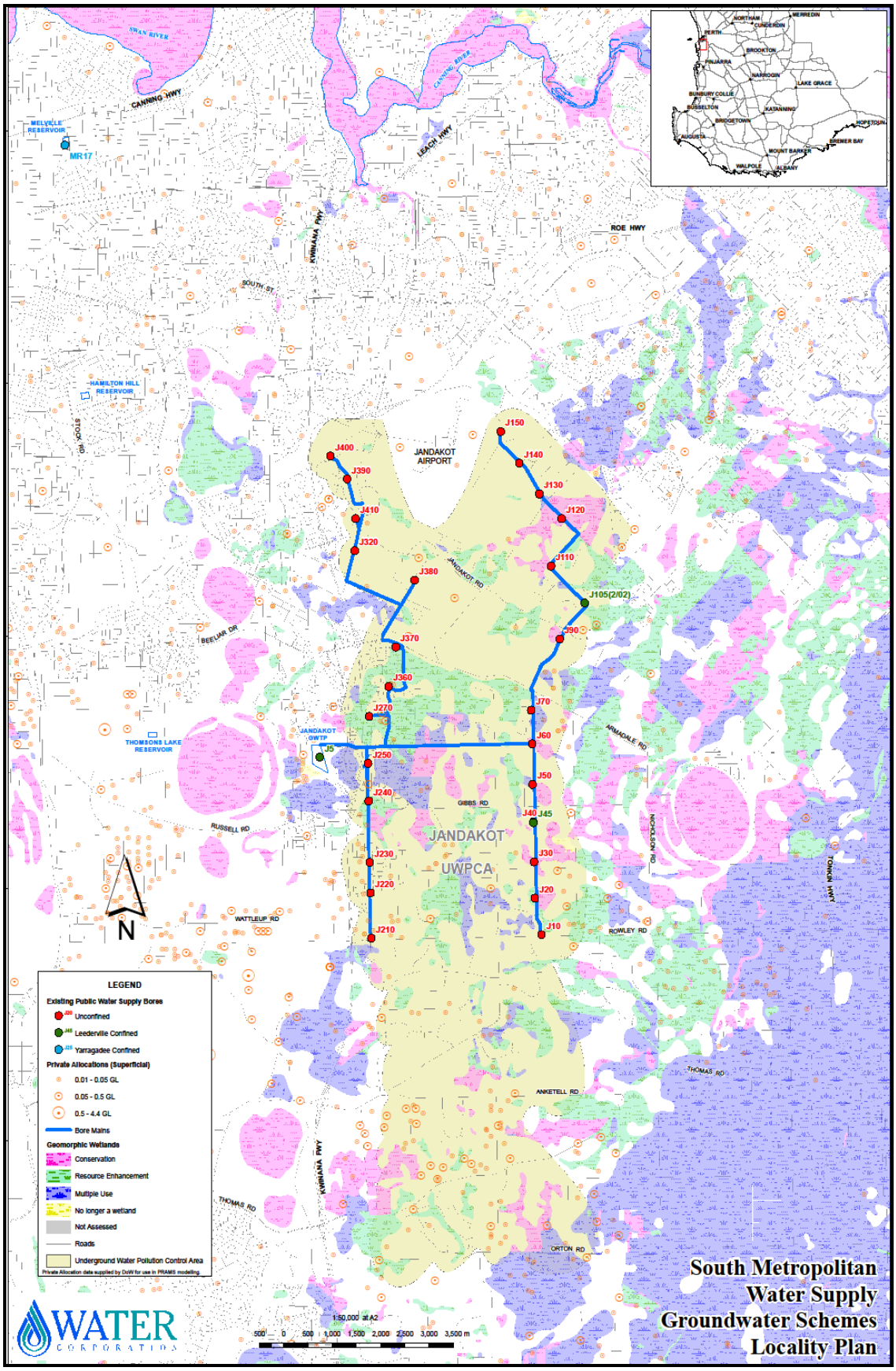


Figure 4 - 2: Plan of the Jandakot Borefield

Table 4 - 1: Averages and ranges of water quality parameters of the groundwater blends before and after some treatment stages over a time period of approximately 3 years (2006 – 2009) (WCWA 2009).

Water Sample		Raw			Filter Inlet (Post-Clarifier)			Filter 1*			Filter 3*		
		Av	Min	Max	Av	Min	Max	Av	Min	Max	Av	Min	Max
DOC concentration (mg L^{-1})		9.6	5.6	25.1	3.1	1.0	4.9	3.0	0.8	4.3	2.9	0.9	4.8
UV_{254} (cm^{-1})		0.46	0.21	0.70	0.08	0.05	0.11	0.08	0.05	0.10	0.07	0.04	0.10
Alkalinity (mg L^{-1} $CaCO_3$)		125	119	134	82	70	113	82	70	112	83	73	113
Bromide concentration (mg L^{-1})		0.76	0.42	1.02	0.93	0.56	1.57	0.91	0.59	1.57	0.92	0.56	1.60
Iron concentration (mg L^{-1})		1.30	0.96	2.0	0.09	<0.02	0.70	0.04	<0.02	0.30	0.05	<0.02	0.55
Temperature (°C)		23.5	21.0	25.5	24.6	21.5	30.2	24.4	21.2	29.4	24.3	21.4	29.4
pH		6.84	6.40	7.10	6.43	6.05	7.42	6.48	6.14	6.82	6.46	6.14	6.78
Chlorine concentration (mg L^{-1})[a]	**Free**	-	-	-	0.36	<0.02	3.80	0.15	<0.02	1.40	0.03	<0.02	0.24
	Total	-	-	-	0.74	<0.02	4.20	0.41	<0.02	1.87	0.08	<0.02	0.62
Monochloramine concentration (mg L^{-1})[b]		-	-	-	0.34	<0.02	1.02	0.21	<0.02	0.95	0.07	<0.02	0.21
Free Ammonia concentration (mg L^{-1})[b]		0.34	0.14	0.55	0.32	<0.02	0.50	0.30	<0.02	0.51	0.30	<0.02	0.48

*Filter 2 has not been included as results are similar to Filter 1

[a] concentration measured directly using chlorine Hach meter

[b] concentration measured directly using monochloramine Hach meter

formation of halogenated organic compounds) and for the option of the application of ozone (due to the potential formation of bromate).

The average dramatic decrease in DOC concentration and UV_{254} absorbance achieved during the clarification process is shown in Table 4-1. Since the type and concentration of NOM (expressed as DOC) is a major factor that controls ozone stability, such removal of DOC is beneficial for the efficiency of an ozonation process. The water samples have a relatively low alkalinity, which is problematic for ozone stability, as low scavenger concentrations (e.g. carbonate/bicarbonate) result in •OH reacting with ozone rather than scavengers, thereby lowering the oxidation capacity in the system (von Gunten 2003b). Unfortunately, iodide concentrations have not historically been measured in this water system.

While the average reductions in DOC concentrations are good, the final DOC concentration in the product water can still be very high (up to 4.8 mg L^{-1}), depending on the inlet raw water DOC concentration. After final disinfection with chlorine, such high product water DOC concentrations result in formation of DBPs which occasionally exceed their respective guideline values. In addition, depending on the bore combination, the product water may be slightly salty (WCWA 2010). As a result, the product water is preferentially mixed in the Lake Thompson reservoir with water from the Perth Seawater Desalination Plant (WCWA 2010), or with lower salinity surface water if the desalination plant is offline, prior to distribution.

4.1.3 Scope of Study

The primary objective of the Jandakot study (described in Chapters 4 – 6) was to determine whether an ozonation step would be beneficial to include in the Jandakot GWTP to enhance NOM and DBP precursor removal, and whether the ozonation step could be optimised to ensure that bromate concentrations remained well below the Australian Drinking Water Guidelines value.

The aim of the study described in this Chapter was to determine the optimal point in the Jandakot treatment system to apply an ozone process; the optimal point being the location at which ozone would be most stable, and therefore both effective and economical to use. This information was required prior to implementation of a pilot

ozonation/biological activated carbon (BAC) process at the Jandakot plant. Further investigations to illustrate the effect of NOM on an ozonation process at the Jandakot GWTP, by comparing ozonation of diluted, untreated raw water with post-clarified water, are also presented in this Chapter.

Chapters 5 and 6 continue the investigation into the effect of an ozonation step on DBP formation in the post-ozonated and product water. The formation of THM4 and bromate, as well as the effect of treatment modifications, such as pH depression and the chlorine-ammonia process, on bromate formation, were investigated in Chapter 5. In addition, the effect of chlorination, both prior to and after the ozonation step, on downstream water chemistry was also examined. The formation of iodo-THMs and iodate in Jandakot GWTP water from ozonation treatment is considered in Chapter 6.

4.2 Experimental

4.2.1 Water Samples

There were two sampling events for the study in this Chapter, as detailed in Table 4-2. The first water samples (S1) were collected on 4th March 2009, a day in which the Jandakot GWTP was producing approximately 20 ML per day of water. Three water samples were collected from different sample points along the treatment process. The untreated raw water sample (R) was collected from a sampling point prior to the first chlorination step, the post-clarified sample (PC) was taken from a sampling point prior to the filters, while the post-filtered sample (PF) was taken from a sampling tap after Filter 3. The second set of samples (S2) was collected on 31st March 2010, a day in which the GWTP was producing approximately 40 ML per day of water. Two water samples were collected: R and PC.

Table 4 - 2: Details of the samples collected from the Jandakot GWTP from the two sampling events

Sampling Event	Production Volume (ML)	Sample Code	Sampling Point
S1	20	R	prior to the first chlorination step
		PC	prior to the filters
		PF	after Filter 3
S2	40	R	prior to the first chlorination step
		PC	prior to the filters

At each sampling point, water samples were collected in 4 L amber glass bottles. Samples were immediately transported back to the laboratory and filtered (0.45 µm membrane) prior to being stored at 4ºC for up to 1 month prior to use in the kinetic experiments comparing the ozone/•OH concentrations after ozonation of waters taken throughout the treatment process, and the experiments comparing ozonation of diluted raw water to post-clarified water.

4.2.2 Solvents and Reagents

All solvents and reagents used in this work were of analytical grade purity (AR grade ≥ 99% pure) or better, with the exception of the aqueous sodium hypochlorite solution (12.5%, technical grade, Ajax Finechem). During the course of the Thesis research, the chlorine stock solution was found to be contaminated with a small amount of bromine and this contamination was considered when analysing the experimental results in this study. Prior to chlorination of water samples, a concentrated solution of NaOCl (approximately 700 mg L^{-1} as Cl_2) was prepared by dilution of the manufacturer's solution with laboratory water. This concentrated NaOCl solution was found to contain 3.7 µg L^{-1} bromate per mg L^{-1} chlorine, and this background bromate contamination was subtracted from bromate concentrations measured in the ozonation experiments. The concentration of chlorine was standardised by measurement of the absorbance of OCl^- at 292 nm (ε = 350 M^{-1} cm^{-1}).

Ozone stock solutions of approximately 34 mg L^{-1} were prepared by continuously bubbling ozone containing oxygen from an ozone generator (American Ozone Systems Inc) through a Dreschel bottle into ice-cooled laboratory water, as described by Bader and Hoigne (1981), and the ozone concentrations of the stock solutions were standardised by measurement of the UV absorbance ($\varepsilon_{258\ nm}$ = 3000 $M^{-1}cm^{-1}$).

4.2.3 Measurement of Water Quality Parameters in Water Samples

4.2.3.1 On-site Chlorine Residual Measurements

Residual chlorine concentrations (free and total) were measured on-site at the Jandakot GWTP using a Hach Pocket Colorimeter (as detailed in Section 3.2.3.1).

4.2.3.2 On-site Chloramine Residual and Ammonia Measurements

Residual chloramine and ammonia concentrations were measured on-site at the Jandakot GWTP using a Hach Pocket Colorimeter (as detailed in Section 3.2.3.2).

4.2.3.3 UV_{254} Absorbance and Specific Ultraviolet Absorbance at 254 nm Measurements

The UV absorbance of the water samples was measured as detailed in Section 3.2.3.3.

4.2.3.4 Dissolved Organic Carbon Analysis

The DOC concentration of the water samples was determined as detailed in Section 3.2.3.4.

4.2.3.5 Alkalinity Measurements

The alkalinity of the waters was measured using Standard Method 2320 B (Clesceri et al. 1998), via titration with sulphuric acid (Ajax Chem) standardised in the laboratory.

4.2.3.6 Bromide, Bromate, and Iodate Ion Measurements

Bromide, bromate, and iodate ions were measured simultaneously via ion chromatography using a Dionex ICS3000 (AG9HC/AS9HC) followed by a post-column reaction, according to the standard operating procedure for an existing method previously reported by Salhi and von Gunten (1999). All samples were measured in duplicate and blank analyses were performed. The limits of detection (LODs) were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004). The average LOD for bromide was 2 µg L^{-1} (25 nM), for bromate was 0.5 µg L^{-1} (4 nM), and for iodate was 1 µg L^{-1} (6 nM).

4.2.3.7 **p-***Chlorobenzoic Acid Measurements*

p-Chlorobenzoic acid (pCBA) was quantified by high performance liquid chromatography (HPLC) (Agilent Technologies 1200 Series) with UV detection at 240 nm. The flow rate and eluent were 0.8 mL min^{-1} of 70% methanol: 30% 10 mM phosphoric acid. The column was a 4.6 mm × 150 mm Eclipse XB8-C18 (Agilent)

5µm particle size, with a pre-column attachment. The LOD was calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004). With a 100 µL injection, the average LOD for pCBA was 3 µg L^{-1}.

4.2.3.8 Ozone Measurements

The concentrations of dissolved ozone in the experimental reaction solutions were determined by the Indigo Method (Bader and Hoigne 1981). Photometric measurements of the residual indigo solution were performed with a UVmini-1240 UV-vis spectrophotometer (Shimadzu) at 600 nm.

4.2.4 Comparison of the Kinetics of the Concentrations of Ozone and •OH after Ozonation of the Water Samples

4.2.4.1 Batch-Type Experiments

All kinetic experiments were carried out at pH 6.5 and 7.5, and all samples were adjusted to the desired pH by adding dilute (0.1 M) hydrochloric acid or sodium hydroxide solutions. An aliquot (500 µL) of a stock solution of pCBA in laboratory water (1 mM) was added to all water samples (500 mL) to achieve initial pCBA concentrations of 0.5 µM prior to ozonation in these batch-type experiments.

Batch-type ozonation experiments were performed by injecting small volumes of ozone stock solution into 500 mL of the prepared water sample in a closed bottle (500 mL) equipped with a dispenser system (Boeco, Germany) similar to that described in Hoigne and Bader (1994). After each specified reaction time, a sample (8 mL) was dispensed into a tube containing buffered indigo trisulphonate (500 µL of 1 mM solution) to quench the ozone reaction and analyse for ozone via the residual indigo absorbance, and to analyse for pCBA. An additional sample (8 mL) was taken for analysis of bromide, bromate and iodate. This sample was quenched with indigo tri-sulphonate without the buffer (75 µL of 10 mM solution) to avoid interference of the buffer ions during the ion chromatographic separation.

4.2.4.2 Comparison of Ozonation of Water Samples Along the Treatment Process

Batch-type ozonation experiments were performed using S1 R, PC, and PF water in order to determine the optimum location of an ozonation step in the Jandakot GWTP. Ozone was added into the water samples (500 mL) in batch-type ozonation

experiments, as detailed in Section 4.2.4.1, to achieve initial ozone concentrations of 3 mg L^{-1} and 6 mg L^{-1}, depending on the rate of ozone consumption of the sample water. Ozone consumption was determined by the amount of time taken for the ozone to be consumed, and the initial ozone concentration chosen with the aim to obtain a decay spanning minutes rather than seconds to enable the kinetic changes to be observed. If the ozone was consumed too rapidly, the experiment was either repeated with more ozone until the decay spanned minutes, or chlorine was added 24 hours prior to ozonation. Chlorine (5 mg L^{-1}) was added to R water (500 mL) and the reaction mixture was stored in the dark for 24 hours, prior to ozone dosing.

4.2.4.3 Comparison of Ozonation of Post-Clarified Waters on Different Production Days, and of Post-Clarified Water to Diluted Raw Water

Batch-type ozonation experiments were conducted with S1 (PC) water and S2 (PC) water in order to compare the performance of ozone on samples taken from different production days, as well as the effect of NOM character. Additional experiments were performed with the S2 (R) water, which was diluted (3.5 × dilution using laboratory water) in order to obtain an equivalent DOC concentration to the S2 (PC) water. This diluted raw water sample will be referred to as 'DR'. The experimental details are shown in Table 4-3. The alkalinity of the DR water was adjusted to the equivalent S2 PC sample alkalinity with sodium bicarbonate prior to ozonation in batch-type experiments, as detailed in Section 4.2.4.1. Ozone was added into the water samples to achieve initial concentrations of 3 mg L^{-1} for all PC samples, and 6 mg L^{-1} for the DR sample. Originally, the initial concentration of ozone of 3 mg L^{-1} was used for the DR sample, however the reaction was too rapid for sampling for kinetic studies, and therefore the initial ozone concentration was doubled.

Table 4 - 3: Experimental details for the comparison of ozonation of the post-clarified (PC) and diluted raw (DR) water samples.

Sampling Event	Production Volume (ML)	Sample Code	Sample Description	Ozone Dose
S1	20	PC	Post-clarified water	3 mg L^{-1}
S2	40	DR	Raw water diluted 3.5 ×	6 mg L^{-1}
		PC	Post-clarified water	3 mg L^{-1}

4.3 Results and Discussion

4.3.1 Characteristics of the Water Samples

Water samples from different sample points along the treatment process at the Jandakot GWTP were collected on two occasions. The combination of bores and their respective production volumes for the two sampling events (S1 and S2) are shown in Figure 4-3. Only three bores (J045, J070, and J105) were operational on both of the two sampling days (i.e. common to the two samples, S1 and S2), and only two of these (J070 and J105) were drawing similar volumes.

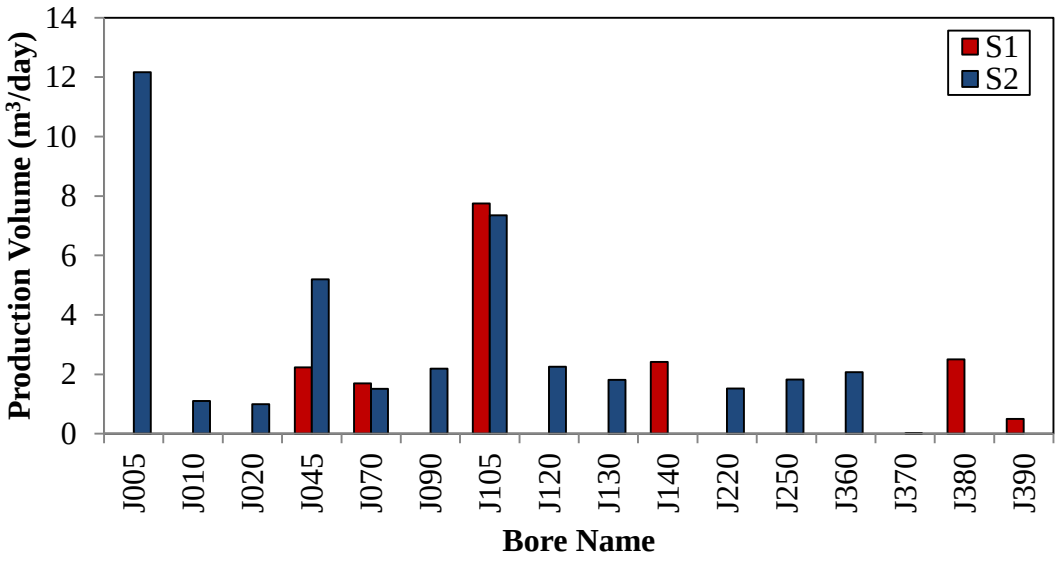


Figure 4 - 3: Bore combination and production volumes for the S1 and S2 sampling days

Some of the water quality parameters of the groundwater blends at the time of sampling are listed in Table 4-4. The two R waters contained very different concentrations of DOC, with the DOC concentration in S2 (R) twice the concentration of DOC in S1 (R). However, the clarification process removed a substantial amount of DOC, resulting in the two PC waters containing similar DOC concentrations, representing the DOC recalcitrant to coagulation for removal. Generally, the water quality of the two PC waters was similar, on the basis of the water quality characteristics that were measured.

Table 4 - 4: Some water quality characteristics of the groundwater blends at the time of sampling events S1 and S2

Water sample		S1			S2	
		R	PC	PF	R	PC
DOC (mg L^{-1})		6.3	3.2	3.1	12.1	3.5
UV_{254} (cm^{-1})		0.21	0.06	0.06	0.6	0.09
$SUVA_{254}$ (L mg^{-1} m^{-1})		3.3	1.9	1.9	5.0	2.6
Alkalinity (mg L^{-1} $CaCO_3$)		119	73	73	143	86
Bromide (mg L^{-1})		1.02	0.90	0.96	0.85	0.94
Temperature (ºC)		24.6	24.3	24.3	24.0	24.8
pH		6.8	6.4	6.7	6.7	6.3
Chlorine (mg L^{-1})	**Free**	-	<0.02	<0.02	-	<0.02
	Total	-	0.35	0.05	-	0.70
Monochloramine (mg L^{-1})		-	0.2	0.05	-	0.43
Free Ammonia (mg L^{-1})		0.45	0.34	0.36	0.30	0.33
Bromate (µg L^{-1})		<0.02	<0.02	<0.02	<0.02	<0.02
Iodate (µg L^{-1})		<2	4.5	4.8	<2	4.1

While these sample waters contained relatively high concentrations of bromide (> 0.8 mg L^{-1}), the alkalinity was relatively low (< 150 mg L^{-1} as $CaCO_3$). The $SUVA_{254}$ value is reported to describe the nature of the NOM in a water sample in terms of hydrophobicity and hydrophilicity, wherein a $SUVA_{254}$ value > 4 indicates the presence of high molecular weight (MW) hydrophobic, especially aromatic, organic matter, a value of 2 – 4 indicates a mixture of hydrophilic and hydrophobic matter of varying MW, and a value of < 2 indicates mainly low MW hydrophilic organic matter (Edzwald and Tobiason 1999). The $SUVA_{254}$ values measured in the R waters were very high, indicating the water blends contained high concentrations of high MW hydrophobic organic matter. The decrease in $SUVA_{254}$ after coagulation and clarification indicates the removal of a high proportion of these NOM structures, resulting in lower $SUVA_{254}$ values, reflecting the presence of predominantly lower MW hydrophilic organic matter. Iodate was present in the post-clarified water samples due to the chlorination step prior to the clarifier resulting in the oxidation of iodide in the raw water to HOI and then to iodate (Bichsel and von Gunten 1999). Bromate, however, is not present throughout the treatment system as neither chlorine nor chloramine (formed *in situ*) have the potential to oxidise HOBr to bromate (von Gunten 2003a).

4.3.2 Comparison of the Kinetics of the Concentrations of Ozone and •OH after Ozonation of the Water Samples

4.3.2.1 Determination of the Optimum Location of an Ozonation Process

With the aim of characterising the ozonation system with respect to the concentrations of ozone and •OH produced in each water, the R_{ct} value (described in Section 4.1.1) was determined for each S1 water sample. The R water was found to have a much higher oxidant demand than the PC water. Ozone was added to the PC and PF waters to achieve an initial concentration of 3 mg L^{-1}, however it was found that the R water required pre-chlorination (5 mg L^{-1}) prior to the ozone dose (3 mg L^{-1}), otherwise the applied ozone dose had to be doubled (6 mg L^{-1}) in order to observe the pCBA oxidation, due to the larger amount of NOM in the R water quickly consuming the ozone. The logarithmic decreases of pCBA vs. the ozone exposure (the ozone concentration integrated over time; $\int[O_3]dt$) for the three water types, including R water with pre-chlorination and the lower ozone dose and R water with the higher ozone dose, at pH 7.5 are presented in Figure 4-4. There are two reaction phases during ozonation, the initial and the secondary, and these are clearly visible in Figure 4-4. The initial phase is indicated by the dotted line, where the ozone consumption is rapid and "instantaneous". In this phase, the R_{ct} value can be 10 times larger than in the secondary phase, and the initial phase contributes a higher proportion of the overall •OH exposure compared to the overall ozone exposure (Elovitz and von Gunten 1999; Elovitz et al. 2000a). Due to the reaction apparatus, it was not possible to acquire kinetic data for the initial phase. The secondary phase is indicated by the solid line in Figure 4-4. Reaction of ozone in this phase follows first-order kinetics and the R_{ct} value is constant for a given set of water quality parameters. It is from this phase that the R_{ct} values shown in Figure 4-4 were calculated.

The R_{ct} of the R water was higher than the PC and PF waters, which is expected due to the high DOC content and low alkalinity of the R water, thereby enhancing ozone decomposition. However, as a higher ozone dose or pre-chlorination was required for the R water, it was difficult to directly compare the differences in R_{ct} between the R and PC/PF samples. The PC and PF waters had similar R_{ct} values, which is expected as the waters were similar in quality. Therefore, the PC and PF waters had similar behaviour in regards to the •OH induced oxidation of pCBA, and the stability of

ozone. This is likely due to the substantial removal of NOM by the addition of alum in the clarification process in the plant, thereby reducing both the R_{ct} value and consumption of ozone by NOM (as a higher NOM concentration results in increased reactions with •OH, and indirectly affects ozone stability (von Gunten 2003b)).

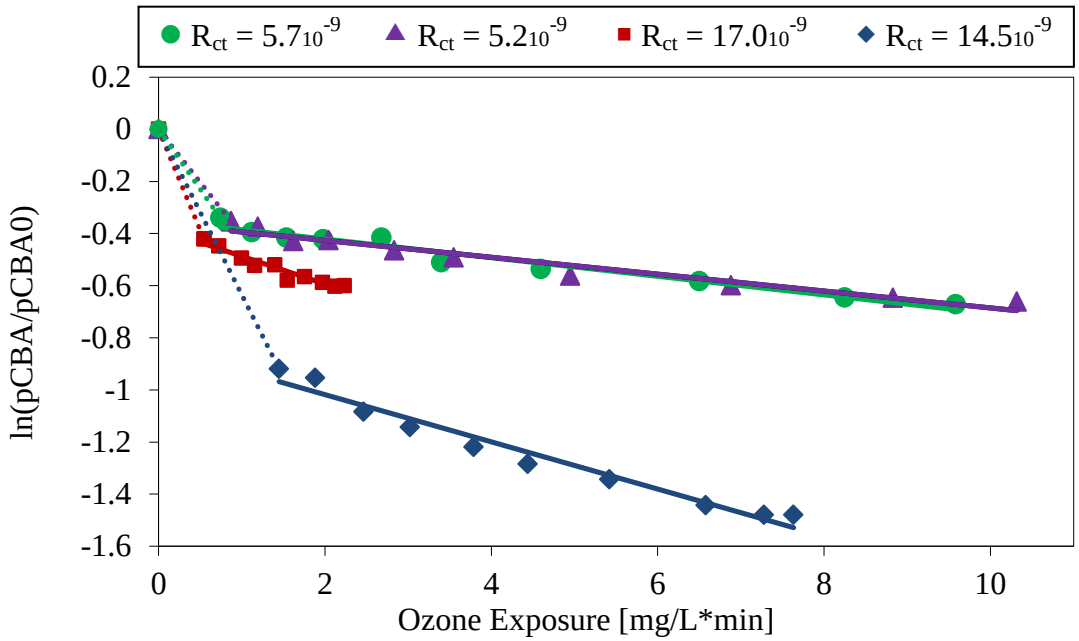


Figure 4 - 4: The •OH induced oxidation of pCBA in Jandakot GWTP water (pH 7.5): PC water dosed with 3 mg L^{-1} O_3 (●); PF water dosed with 3 mg L^{-1} O_3 (▲); 5 mg L^{-1} pre-chlorinated R water dosed with 3 mg L^{-1} O_3 (■); and R water dosed with 6 mg L^{-1} O_3 (◆)

As ozone was less stable in the R water, and a higher ozone dose was required to reach an ozone residual concentration, it would be more economical to place an ozonation step after the clarification process, a process in which a large proportion of NOM is removed. The increased ozone stability at the PC or PF points in the treatment process would also be beneficial for DBP control as it would allow more direct ozone reactions to occur, thereby resulting in the transformation of high MW organic matter into lower MW organic matter, and decreasing potential DBP precursors. In addition, due to ozonation of NOM leading to the formation of biodegradable organic compounds, which could allow bacterial regrowth and result in a negative impact on the water quality in the distribution system (Hammes et al.

2006), it was determined that the optimum location for the ozonation step would be post-clarification but before the filtration step, so that any biodegradable DOC (BDOC) formed by ozonation could be removed in the existing filtration process or an improved filtration process.

4.3.2.2 Comparison of Ozonation of Raw and Post-Clarified Water Samples

In order to compare the characteristics of the R and PC waters during ozonation, S2 (R) water (DOC: 12.1 mg L^{-1}) was diluted (× 3.5) in order to obtain an equivalent DOC concentration to the corresponding S2 (PC) water (DOC: 3.5 mg L^{-1}). The impact of the type of NOM on ozonation of the diluted R (DR) and PC waters were assessed, as well as the concentration of bromide and formation of bromate and iodate.

4.3.2.2.1 Impact of NOM on Ozonation

Although the DR and PC samples had equivalent DOC concentrations, it appears that the type of organic components within the waters was very different. As with the experiment in Section 4.3.2.1, the DR sample required twice the ozone dose applied to the PC sample in order to allow sufficient time for kinetic analysis of the decay of ozone. Table 4-5 gives the R_{ct} values for the second phase of ozonation for the S1 and S2 PC samples, and the S2 DR sample, at pH 6.5 and 7.5.

Table 4 - 5: R_{ct} values for the second phase of ozonation

Sample Water	Ozone Dose	pH 6.5	pH 7.5
S1 (PC)	3 mg L^{-1}	2.5 x 10^{-9}	5.6 x 10^{-9}
S2 (PC)	3 mg L^{-1}	2.0 x 10^{-9}	5.8 x 10^{-9}
S2 (DR)	6 mg L^{-1}	27.8 x 10^{-9}	52.8 x 10^{-9}

It can be seen from Table 4-5 that the PC samples from the two different production days appeared to behave similarly in their •OH and ozone chemistry, as shown by the similar R_{ct} values for these two samples at both pH 6.5 and 7.5 for the second phase of ozonation. It can therefore be inferred that the NOM composition between the two waters was also similar, likely to be a result of the coagulation and clarification process being unable to remove a recalcitrant fraction of NOM of fairly consistent nature. The dramatic increase in R_{ct} observed for the DR water is likely to be due to the increased concentration of applied ozone (6 mg L^{-1}) compared to the PC waters

(3 mg L^{-1}), resulting in a higher ozone exposure. The additional ozone requirement indicates the presence of organic matter and inorganic constituents which are highly reactive with ozone within the DR water sample. The effectiveness of the coagulation and clarification process in the removal of this ozone-reactive NOM is also apparent from the R_{ct} values in Table 4-5. The similar R_{ct} values for the two PC waters show that the S1 and S2 water samples, which contained significantly different DOC concentrations in their R water blends, had much more similar NOM characteristics after clarification (Table 4-4). This finding is also supported by the similar SUVA values of these two PC samples.

The influence of the nature of NOM on ozonation treatment was shown by Elovitz et al. (2000a), who demonstrated the differences in ozonation reaction rates which can result from NOM originating from different source waters (i.e. lakes, groundwaters, and rivers). They surveyed 12 waters in Switzerland, and found the ozone decay rates and R_{ct} values ranged over two orders of magnitude, with a mean R_{ct} value of 1.56 ($\pm$ 1.6) $\times 10^{-8}$ when a 1 mg L^{-1} ozone dose was applied. In their study, 6 of the waters had similar DOC concentrations (1.2 $\pm$ 0.2 mg L^{-1}) and alkalinity (205 $\pm$ 25 mg L^{-1} $CaCO_3$), but they still found a 3-fold difference in ozone depletion rates and an order of magnitude variation in R_{ct} values (Elovitz et al. 2000a).

In the current study, the effect of the nature of the NOM on the R_{ct} values is shown by the 10 fold difference between the R_{ct} of the DR sample and its respective PC sample. In addition, the observed similarity in water quality after the clarification process for different water blends, as reflected by the similar S1 and S2 PC R_{ct} values, would be advantageous for location of an ozone treatment process post-clarifier at the Jandakot GWTP. Similar R_{ct} values, despite different production volumes and bore combinations, would indicate the ozone consumption would be similar on different production days, and therefore the ozonation process would be stable and not require extensive or complicated operator control.

4.3.2.2.2 Impact of NOM on Bromate Formation during Ozonation

The Australian Drinking Water Guidelines set the maximum level of bromate permissible in treated water at 20 µg L^{-1} (NRMMC-NHMRC 2011). Since the blended groundwaters feeding the Jandakot GWTP contain high bromide

concentrations (Table 4-1), it was important to assess the formation of bromate in the Jandakot samples. The bromate concentrations were measured during the batch-type experiments, as described in Section 4.2.4.1. The formation of bromate during the ozonation of the S2 (PC) and (DR) samples at pH 6.5 and 7.5 is shown in Figure 4-5.

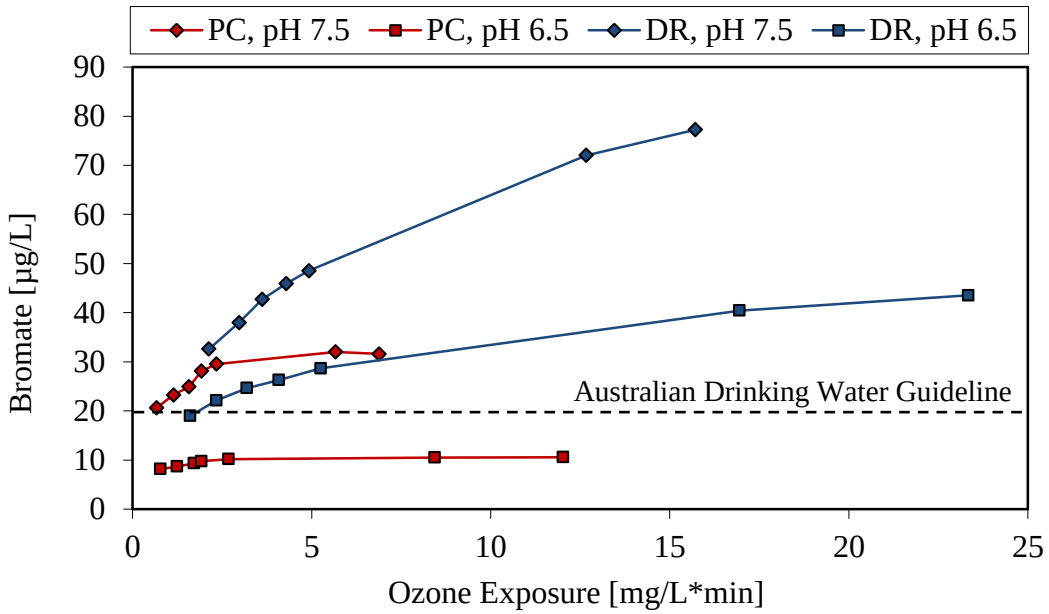


Figure 4 - 5: Bromate formation during ozonation of S2 samples (ozone doses: PC = 3 mg L^{-1}; DR = 6 mg L^{-1}) at pH 6.5 and 7.5 (bromate concentration in the chlorine stock solution has been subtracted). The Australian Drinking Water Guidelines value for bromate is indicated by the dashed line

The formation of bromate during ozonation of bromide-containing water will be reviewed and explored in more depth in Chapter 5. In summary, there are two stages to bromate formation: the fast initial increase, mostly due to •OH reactions; and the slower formation in the secondary phase, due to both ozone and •OH reactions. These stages are apparent in Figure 4-5, particularly in the PC water (red markers), in which there was a fast increase in bromate, followed by a slower formation which eventually ceased as the •OH were consumed, resulting in the plateau. In comparison, the DR water shows a prolonged bromate formation over the reaction period, likely due to the higher ozone dose, the relative amount of •OH formation, and how these oxidants reacted within the diluted water matrix. The effect of pH is also clear, with pH 7.5 resulting in higher concentrations of bromate, due to the higher decomposition rate of ozone by hydroxide at the higher pH, resulting in

increased •OH concentrations (von Gunten 2003b) (as described in Section 2.2.1), as well as increased concentrations of HOBr (see Section 5.1.1. for more detail). The effect of pH on bromate formation in the Jandakot PC samples will be further explored in Chapter 5.

Interestingly, despite the fact that the DR water contained a lower initial concentration of bromide due to the 3.5 times dilution of the R water, the resulting bromate formation from the DR water was higher than that observed in the PC water. The residual bromide concentrations, after quenching of the oxidant residual, were measured during the batch-type experiments, as described in Section 4.2.4.1. Figure 4-6 presents the residual bromide concentrations of the PC and DR waters. It can be seen that the initial bromide concentration in the DR water was 3.5 times lower than the bromide concentration in the PC water, as expected from the dilution of the R water. The higher bromate concentration from the DR water was likely to be due to the differences in NOM compared to the PC water, as well as the higher ozone dose applied to the DR water, allowing for a higher exposure to ozone and •OH and thus increased bromate formation. Yield calculations were performed using the initial bromide concentration and the final bromide concentration, analysed after quenching of the oxidant residual at the end of the batch-type experiments. It was found that the higher ozone dose for the DR water resulted in a larger percentage decrease in the bromide concentration upon ozonation. The residual bromide concentrations during ozonation of the PC and DR samples at pH 6.5 and 7.5 are shown in Figure 4-6. When 3 mg L^{-1} ozone was applied to PC water, the initial decrease in bromide was approximately 5%, however the 6 mg L^{-1} ozone dose applied to the DR water resulted in an approximately 30% decrease in bromide. Interestingly, the percentage of bromide converted into bromate was similar between the two waters, and depended on the pH of the experiment. It is therefore apparent that, in the DR sample, a higher percentage of the initial bromide remains unaccounted for compared to the PC sample, and it is expected that this portion of the bromide was converted into organic brominated-DBPs. In addition, yield calculations were performed using the initial bromide concentration and the initial phase bromate concentration, taken within the first 30 seconds of the batch-type experiment. It was found that at pH 7.5, the percentages of bromide converted into bromate in the PC and DR water were 25% and 27%, respectively, and at pH 6.5 were 11% and 17%, respectively. This

shows the initial rate of bromate formation was similar between the PC and DR waters.

Figure 4-5 also shows that, with the exception of the PC water at pH 6.5, the Australian Drinking Water Guidelines bromate value was exceeded. As the average pH at the Jandakot GWTP is 6.4 (Table 4-1), it can be assumed that the Australian Drinking Water Guidelines value should not be exceeded if ozone doses < 3 mg L^{-1}

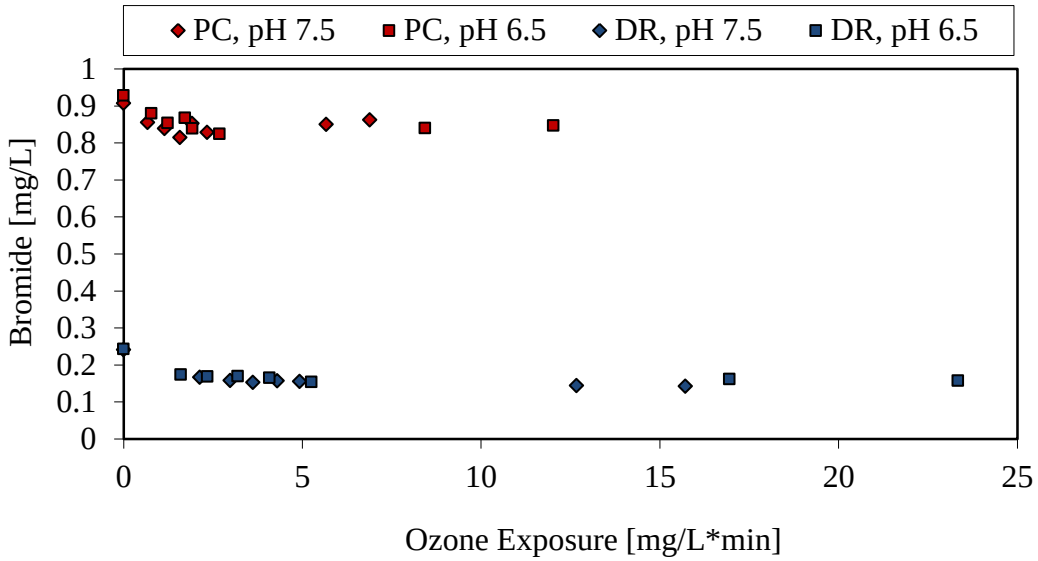


Figure 4 - 6: Residual bromide concentrations during ozonation of S2 samples (ozone doses = PC: 3 mg L^{-1}; DR: 6 mg L^{-1}) at pH 6.5 and 7.5

are applied. However, this result also shows the probability of higher bromate formation should the water quality post-clarifier alter during ozone treatment in regards to pH or DOC character. In comparison, the bromate formation from DR water at pH 6.5 after the complete reaction time was approximately double the Australian Drinking Water Guidelines value. This reinforces the negative consequences of requiring a high ozone dose in order to compensate for the reactivity of the NOM in bromide-containing waters. It also highlights the fact that ozone should not be applied directly to the raw water blends at the Jandakot WTP, and that pre-treatment of the water (e.g. coagulation and clarification) is required to minimise the ozone dose and cost of the process, as well as the formation of bromate.

4.3.2.2.3 Impact of NOM on Iodate Formation during Ozonation

Naturally occurring iodide can be oxidised by ozone to form hypoiodous acid (HOI), which is rapidly oxidised further by ozone to iodate. Unlike bromate, iodate formation, rather than organic I-DBP formation, in drinking waters is preferable for the drinking water industry, as iodate is nontoxic (it is often added to food for human and animal health benefits) (Burgi et al. 2001), and does not have a drinking water guideline value. While some organic I-DBPs have an undesirable taste and odour (Hansson et al. 1987), it has recently been reported that organic I-DBPs are more toxic than their brominated or chlorinated analogues (Richardson et al. 2008). The formation of iodate and organic I-DBPs during the ozonation of Jandakot GWTP water will be explored in more depth in Chapter 6.

The iodate concentrations were measured during the batch-type experiments, as described in Section 4.2.4.1. The formation of iodate during the ozonation of the S2 (PC) and (DR) samples at pH 6.5 and 7.5 is shown in Figure 4-7. As in Figure 4-5, a fast initial increase followed by a slow increase during the secondary phase of ozonation can be seen. Unlike the bromate formation, iodate formation from the DR sample did not exceed the iodate formation observed in the PC sample under the same pH conditions. Interestingly, the observed iodate concentrations from the DR sample were higher than expected as they did not reflect the 3.5 times dilution when compared to the PC sample. Unfortunately, iodide concentrations were not available for these samples because, at the time, an analytical method with the required sensitivity and reliability was not available, so it was not possible to determine the proportion of the iodide which was converted into iodate, nor the portion which was transformed into iodo-organic DBPs. Iodate formation in the Jandakot PC water is investigated further in Chapter 6.

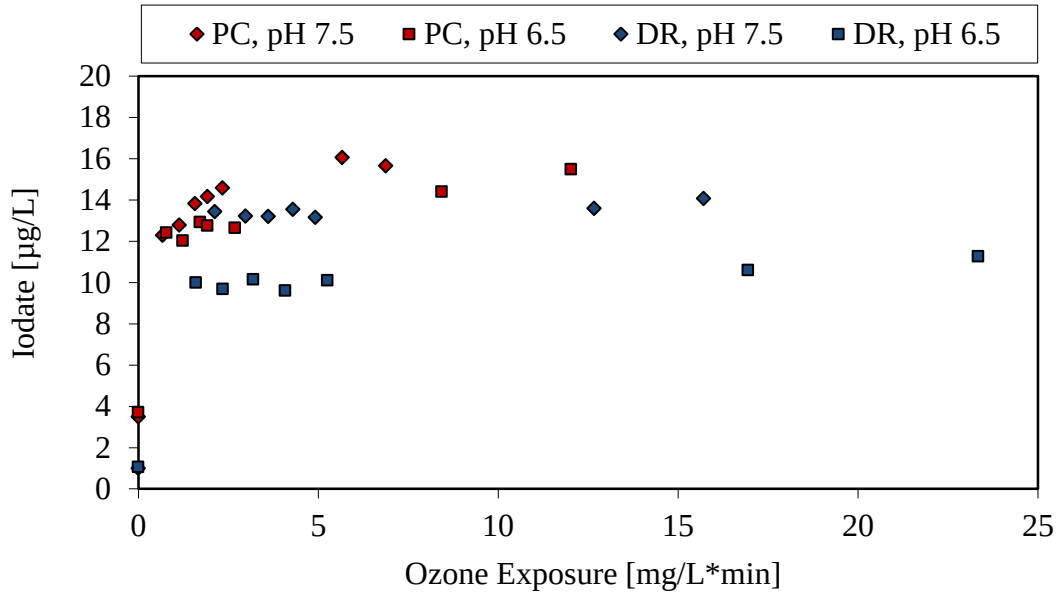


Figure 4 - 7: Iodate formation during ozonation of S2 samples (ozone doses = PC: 3 mg L^{-1}; DR: 6 mg L^{-1}) at pH 6.5 and 7.5

4.4 Conclusions

The effect of the water quality is extremely important when considering where to place an ozonation step in the drinking water treatment process. The experiments in this study were primarily designed to determine the most efficient and beneficial placement of an ozonation process for the enhancement of NOM and THM precursor removal at the Jandakot GWTP, via the determination of where the ozone would be stable enough to enable both ozone and •OH reactions to occur. For samples taken at different stages of the treatment process, the ozone decomposition was assessed and R_{ct} values were determined in laboratory batch experiments. The R water sample had a significantly higher R_{ct} value compared to the PC and PF samples, and required double the ozone dose of the treated samples (PC and PF), unless the R water was pre-chlorinated prior to ozonation thereby altering the DOC character of the R water and rendering it less reactive to ozone.

Comparison of the R_{ct} values between the two PC waters on the S1 and S2 sampling days also showed that the clarification process stabilised the waters, rendering the waters to be of similar quality. The quality of the water post-clarification compared to the raw water was such that the performance of ozone would be significantly improved in the post-clarification water. Bromate formation from ozonation of PC water at pH 6.5 was shown to be below the Australian Drinking Water Guidelines,

while bromate formation from PC water at pH 7.5 and diluted raw water (DR) at pH 6.5 and 7.5 was found to be above the Australian Drinking Water Guidelines. While the average pH of the Jandakot GWTP water in the current study was 6.4, alteration in the pH or water quality could result in bromate concentrations above the guideline value of 20 µg L^{-1}. The need for pre-treatment prior to an ozonation step was reinforced by the high bromate formation observed in the DR water, where the concentration of bromate after the complete reaction time was approximately 40 µg L^{-1}.

It was therefore determined that an ozonation step would be best located between the clarification process and filtration. With the ozonation step in this location, the required ozone dose would be lower than for the raw water because a significant amount of NOM has been removed during coagulation, providing a more economical option. Converting the existing filtration stage into a biological filtration step following ozonation should remove biodegradable organic ozonation products, resulting in increased water quality and a decrease in DBP formation upon chlorination for disinfection at the end of the treatment process. Prior to any implementation, all the processes would need to be optimised with regards to pH, additional chlorination prior to ozonation, and bromate formation, and prepared for adjustment according to the DOC character of the raw water in use.

Chapter 5

THM AND BROMATE FORMATION FROM A WATER CONTAINING HIGH BROMIDE CONCENTRATIONS DURING MULTISTEP TREATMENT WITH CHLORINE AND OZONE

5.1 Introduction

5.1.1 Ozone for Drinking Water Treatment

As discussed in Chapters 1, 2, and 4, ozone is widely used in the treatment of drinking water for several purposes, including disinfection, improvement of colour, taste and odour aspects, oxidation of micropollutants, and the formation of biodegradable organic matter for removal by biological activated carbon filtration (Camel and Bermond 1998; von Gunten 2003b). Ozone is unstable in water, and the rate of ozone decay depends on several factors, such as the concentrations of natural organic matter (NOM) and carbonate/bicarbonate ions, pH, and temperature (Elovitz et al. 2000a). Compared to chlorine, ozone has the advantage in that it does not produce significant amounts of trihalomethanes (THMs) or other chlorinated disinfection by-products (DBPs). The US Environmental Protection Agency (US-EPA) regulates the sum of four THMs (THM4) at 80 µg L^{-1} (US-EPA 2001), and the European Union (EU) regulates THM4 at 100 µg L^{-1} (EU 1998). The Australian Drinking Water Guidelines have set the maximum level of the same four THMs in treated water to 250 µg L^{-1} (NRMMC-NHMRC 2011).

The utilisation of water containing elevated concentrations of DOC and bromide for drinking water purposes in Western Australia can sometimes result in DBP formation in excess of guideline values upon final disinfection. Introducing an ozonation step, followed by a biological treatment process, into established drinking water treatment processes would decrease the formation of the majority of the regulated DBPs upon final disinfection. However, the elevated concentrations of bromide would likely result in the formation of other, potentially more harmful, bromo-DBPs upon ozonation. Therefore, optimisation of any ozonation process with regards to DBP formation is important.

5.1.2 Significance of Bromide in Ozonation Processes

It is well known that when bromide is present in drinking water source waters, hypochlorous acid (HOCl) or ozone can oxidise bromide to hypobromous acid (HOBr). HOBr reacts with NOM to form bromo-organic compounds, some of which have been identified as Br-DBPs (Richardson et al. 1999b). The formation of Br-DBPs is of concern as many Br-DBPs have been shown to be more harmful to human health and stronger carcinogens and mutagens than their chlorinated

analogues (Nobukawa and Sanukida 2001; Echigo et al. 2004; Bull et al. 2006; Richardson et al. 2007). While compared to chlorination, ozonation does not produce significant concentrations of various regulated DBPs, it has been found that, during ozonation, bromate (BrO_3^-) and other Br-DBPs are generated (Richardson et al. 2000; von Gunten 2003b). At present, the application of ozone is occasionally limited by the formation of bromate, which has been classified by the US-EPA as a probable human carcinogen (B2) (US-EPA 2006). The bromate drinking water guideline value in the USA and Europe is set at 10 µg L^{-1} (EU 1998; US-EPA 2006; WHO 2008), and in Australia is set at 20 µg L^{-1} (NRMMC-NHMRC 2011).

Depending on bromide and NOM concentrations, ozone dose, pH, and alkalinity, the concentrations of bromate reported in drinking water typically range from < LOD to ~130 µg L^{-1} (von Gunten and Salhi 2003; Xie and Shang 2006, and references therein) . The mechanism for bromate formation during ozonation is complex and involves both ozone and •OH (von Gunten 2003a). Reaction of bromide with •OH results in Br• formation, which can either react further with ozone to form BrO•, which will disproportionate into hypobromite ions (OBr^-) and BrO_2^-, or react with bromide to form $•Br_2^-$ and eventually form HOBr. Reaction of bromide with ozone will form HOBr/OBr^-. HOBr/OBr^- are important intermediates as both species will react with •OH at similar rates, while ozone will only react with OBr^-. As HOBr has a pK_a of 8.8 (Haag and Hoigne 1983), at pH 7 – 8 HOBr is the dominant species, resulting in the •OH pathway being the major pathway. Reaction of HOBr/OBr^- with •OH produces BrO•, while the reaction of OBr^- produces BrO_2^- (von Gunten 2003a). Once formed, BrO_2^- reacts with ozone to form bromate.

To comply with the bromate regulations, ozone processes used in drinking water treatment must be carefully optimised for waters with elevated bromide concentrations. There are, however, methods to minimise bromate formation, such as the addition of acid (pH depression) or the addition of ammonia (Pinkernell and von Gunten 2001). The chlorine-ammonia process is an additional option for enhanced bromate minimisation (Buffle et al. 2004; Neemann et al. 2004). Depression of pH displaces the HOBr/OBr^- equilibrium towards HOBr, thereby slowing oxidation by ozone. Furthermore, the ozone exposure relative to •OH formation is increased, lowering the R_{ct} value (the ratio of •OH exposure to ozone exposure) and decreasing

the importance of the •OH-based processes. Ammonia addition masks HOBr as monobromamine (NH_2Br), which then reacts slowly with ozone to form NO_3^- and Br^- (von Gunten and Hoigne 1994). The chlorine-ammonia process consists of pre-chlorination followed by addition of ammonia prior to ozonation and, compared to ammonia only addition, has been shown to be more efficient at bromate minimisation, with a 4-fold decrease in bromate formation (Buffle et al. 2004).

5.1.3 Scope of Study

The aim of the study described in this Chapter was to explore ozone as an additional treatment option which could be included in the Jandakot Groundwater Treatment Plant (GWTP). As described in Section 4.1.2, the Jandakot GWTP treats water drawn from a series of bores, with the resulting raw water containing high concentrations of dissolved organic carbon (DOC) (5.6 – 25.1 mg L^{-1} (Table 4-1, Section 4.1.2)) and bromide (0.42 – 1.02 mg L^{-1} (Table 4-1, Section 4.1.2)). The present treatment process utilises pre-chlorination, coagulation, and filtration prior to final disinfection with chlorine. As discussed in Chapter 4, the optimal location for an ozonation step was found to be prior to the filtration process. In the current study, presented in this Chapter, the effect of ozonation or pre-chlorination/ozonation on the formation of the regulated THMs and bromate from water samples obtained prior to the Jandakot GWTP filtration step was studied. The effectiveness of a bromate control method, known as the chlorine-ammonia process, was also investigated. Experiments using the model compound resorcinol were undertaken in order to explain trends observed in the real water experiments.

5.2 Experimental

5.2.1 Water Samples

There were three sampling events in the study in this Chapter, and all samples were taken from a sampling point prior to the filters (post-clarified (PC) water) at the Jandakot GWTP. The first water samples (S1) were collected on 4th March 2009, a day on which the Jandakot GWTP was producing approximately 20 ML per day of water (pre-clarifier chlorination = 6.6 mg L^{-1}; PC DOC = 3.5 mg L^{-1}). The second water samples (S2) were collected on 5th November 2009, a day on which the Jandakot GWTP was producing approximately 30 ML per day of water (pre-clarifier chlorination = 8.0 mg L^{-1}; PC DOC = 2.0 mg L^{-1}). The third water samples (S3)

were collected on 31st March 2010, a day on which the Jandakot GWTP was producing approximately 40 ML per day of water (pre-clarifier chlorination = 18.7 mg L^{-1}; PC DOC = 3.2 mg L^{-1}).

At each sampling event, water samples were collected in 4 L amber glass bottles. Samples were immediately transported back to the laboratory and filtered (0.45 µM membrane) prior to being stored at 4ºC for up to 1 month prior to use in the experiments.

5.2.2 Solvents and Reagents

All solvents and reagents used in this work were of analytical grade purity (AR grade ≥ 99% pure) or better, except for the aqueous sodium hypochlorite solution (12.5%, technical grade, Ajax Finechem). The chlorine stock solution was contaminated with a small amount of bromine and this contamination was considered when analysing the experimental results in this study. Prior to chlorination of water samples, a concentrated solution of NaOCl was prepared (10 mM). This solution contained 3.7 µg L^{-1} bromate / mg L^{-1} chlorine, and this contamination was subtracted from all bromate analyses in these experiments. The concentration of chlorine was standardised by the measurement of the absorbance of OCl^- at 292 nm (ε = 350 M^{-1} cm^{-1}).

Ozone stock solutions of approximately 0.7 mM were prepared using the method detailed in Section 4.2.2.

HOBr experiments were performed using a HOBr stock solution prepared from 3 mM chlorine and 3.3 mM bromide, and the concentration was standardised by the measurement of the UV absorbance of OBr^- at 329 nm (ε = 332 M^{-1} cm^{-1}) at pH 11.

Resorcinol was purchased from Sigma-Aldrich (Castle Hill, NSW). Model compound stock solution (10 mM carbon L^{-1}) was prepared in laboratory water. Aliquots of the model compound stock solution were added into the reaction solution to achieve a concentration of 10 µM carbon L^{-1} (0.12 mg carbon L^{-1}) and the reaction solution was then buffered with 0.12 M phosphate buffer (pH 7) prior to chlorine addition.

5.2.3 Measurement of Water Quality Parameters in Water Samples

5.2.3.1 Chlorine Residual Measurements

Residual chlorine concentrations (free and total) were measured using a Hach Pocket Colorimeter (as detailed in Section 3.2.3.1).

5.2.3.2 Chloramine Residual and Ammonia Measurements

Residual chloramine and ammonia concentrations were measured using a Hach Pocket Colorimeter (as detailed in Section 3.2.3.2).

5.2.3.3 UV_{254} Absorbance and Specific Ultraviolet Absorbance at 254 nm Measurements

The UV absorbance was measured as detailed in Section 3.2.3.3.

5.2.3.4 Dissolved Organic Carbon Analysis

The DOC concentration was determined as detailed in Section 3.2.3.4.

5.2.3.5 Bromide, Bromate, and Iodate Ion Measurements

Bromide, bromate, and iodate ions were measured as detailed in Section 4.2.3.6.

5.2.3.6 **p-***Chlorobenzoic Acid Measurements*

p-Chlorobenzoic acid (pCBA) was quantified as detailed in Section 4.2.3.7.

5.2.3.7 Ozone Measurements

The concentrations of dissolved ozone in the experimental reaction solutions were determined as detailed in Section 4.2.3.8.

5.2.3.8 Solid-Phase Microextraction / Gas Chromatography-Mass Spectrometric Analysis of Chloro- and/or Bromo- THMs

Four chloro- and/or bromo-THMs (chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$) (THM4)) were analysed using the standard operating procedure for an existing method previously reported by Allard et al. (2012). All samples were analysed in duplicate and blank samples were also analysed.

Briefly, an aliquot (10 µL) of an internal standard solution (5 mg L^{-1} 1,2-dibromopropane in methanol) was added directly into the sample (10 mL) contained in a 20 mL sample vial. Sodium sulphate (~5.5 g Na_2SO_4) (Ajax Finechem) was then added and the vial was capped. Headspace solid-phase microextraction (SPME) (using a divinylbenzene/carboxen/polydimethylsiloxane fibre (Supelco®)) was followed immediately by analysis using gas chromatography with mass spectrometric detection (GC-MS) (an Agilent Technologies Series II GC 6890N interfaced to an Agilent Technologies 5973N Mass Selective Detector) with a 30 m x 0.25 mm ID ZB-5 (Phenomenex®) column with a film thickness of 1 µm.

The limits of detection (LODs) were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004) by using the standard deviation of replicate analyses (n = 3) of standard solutions of 200, 1000, and 5000 ng L^{-1} concentration. The average LOD for $CHCl_3$ was 4.3 µg L^{-1} (36 nM), while for $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$, the LODs were 3.5 µg L^{-1} (21, 17 and 14 nM, respectively).

5.2.4 Procedures for Various Ozonation Experiments on Post-Clarified Water Samples, Including Pre-Treatments, Variation of Initial Ozone Concentration, and Post-Chlorination

All experiments were carried out at pH 6.5 and 7.5, and the samples were adjusted to the desired pH by adding dilute (0.1 M) aqueous hydrochloric acid or sodium hydroxide solutions.

For all experiments involving 24 hour chlorination, sodium hypochlorite solution was added to achieve the desired concentration, and the solution was kept in the dark for 24 hours.

5.2.4.1 Comparison of the Kinetics of Ozonation Pre-Treatments On Post-Clarified Water Samples

All kinetic experiments were performed using the batch-type experiments detailed in Section 4.2.4.1. Briefly, batch-type ozonation experiments were performed by adding an aliquot of pCBA solution to all water samples prior to ozonation, after which small volumes of ozone stock solution were injected into the water sample in a closed bottle with a dispenser system. After specified reaction times, two samples were dispensed into tubes containing indigo trisulphonate solution to quench the ozone reaction. The first tube sample was used for the analysis of ozone (via the reduction of indigo trisulphonate, as described in Section 4.2.3.8) and pCBA, and the second tube sample was used for the analysis of bromide, bromate, and iodate.

The basic design of the pre-treatments for the water samples in the kinetic experiments is shown in Figure 5-1 (red boxes). Briefly, the PC samples (S1, S2, and S3) were subjected to pre-chlorination treatment, in which they were chlorinated (0 – 4 mg L^{-1} (0 – 56 µM) as Cl_2) 24 hours prior to ozonation. The S3 PC sample was also given chlorine-ammonia treatment two minutes prior to ozonation, where chlorine was added ten minutes before the ammonia. As ammonia was already present in the sample (approximately 0.34 mg L^{-1} (20 µM) as NH_3), additional ammonia (0.44 mg L^{-1} (26 µM) as NH_3) was added in order to produce a total ammonia concentration equivalent to the concentration of added chlorine (4 mg L^{-1} (56 µM) as Cl_2). The initial ozone concentration used in all experiments was 3 mg L^{-1} (62 µM).

5.2.4.2 Effect of the Initial Ozone Concentration, With and Without Pre- and Post-Treatment, on THM and Bromate formation

The basic scheme of the pre-treatments of the water samples for the initial ozone concentration experiments is shown in Figure 5-1 (purple boxes). The initial pre-treatment experimental conditions were the same as those described in Section 5.2.4.1. Upon ozone addition, the solutions were mixed for 10 seconds, and then divided into two parts (250 mL) in order to prepare samples with and without post-treatment. Post-treatment involved the addition of chlorine (6 mg L^{-1} (85 µM) as Cl_2) 1 hour after ozone addition. These solutions were sub-sampled into 40 mL vials with Teflon-lined caps (duplicate vials for later THM analysis) for samples after pre-treatment/ozonation, as well as post-treatment, and 10 mL plastic test tubes with caps

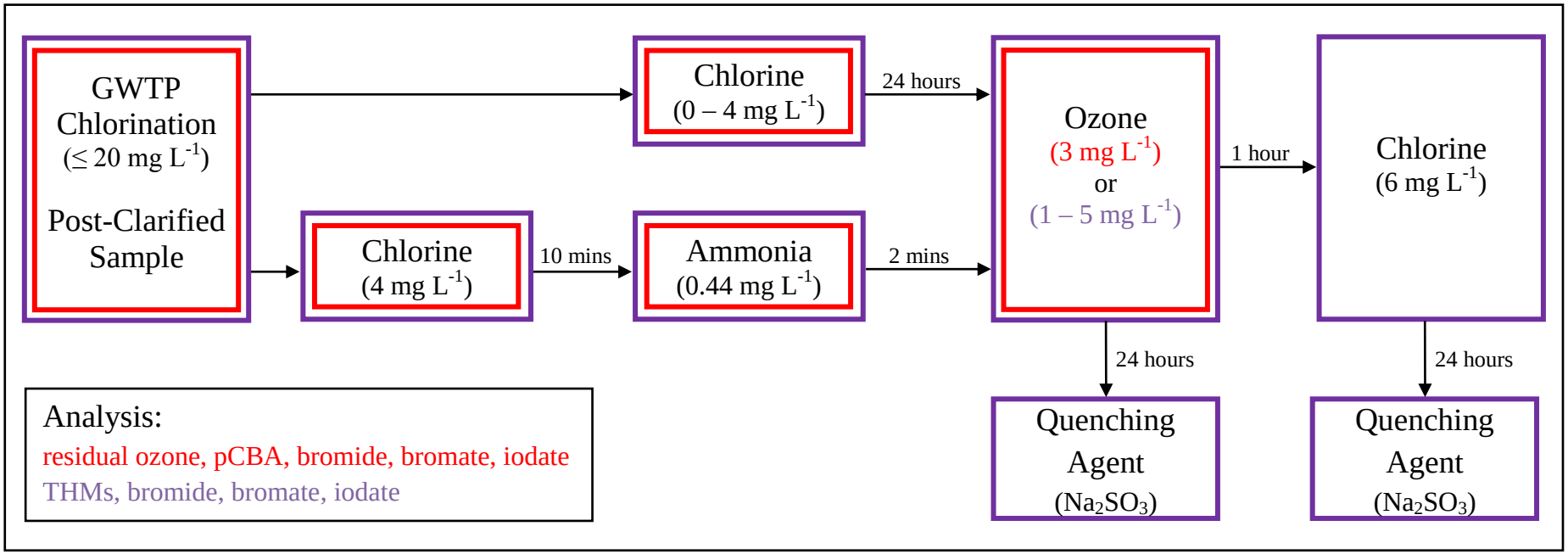


Figure 5 - 1: Schematic of the design of the 'comparison of kinetics of ozonation pre-treatment' experiments (red boxes) and 'effect of initial ozone concentration, with and without pre- and post-treatment, on THM and bromate formation' experiments (purple boxes). Pre-treatments applied to the GWTP post-clarified samples prior to the ozone were pre-chlorination and the chlorine-ammonia process. The post-treatment applied to half the volume of the ozonated samples was post-chlorination. Experiments were performed at pH 6.5 and 7.5

(for later bromide, bromate, and iodate analysis) for samples after pre-treatment/ozonation only. All vessels were filled so that they had no headspace, and were stored in the dark.

The residual chlorine in the 40 mL vials was quenched with a calculated aliquot of an aqueous sodium sulphite solution (21 mM) such that the quenching agent added was 5 times the molar concentration of the initial disinfectant concentration. Samples without post-treatment were quenched 24 hours after ozonation (for experimental consistency and comparison with post-treatment), while samples with post-treatment were quenched 24 hours after post-chlorination. The quenched samples were then stored at 4ºC prior to THM analysis. The plastic test tubes did not require a quenching agent, as the reactions to form these DBPs ceased once the ozone had been consumed.

5.2.5 Comparison of THMs and Bromate Produced from the Chlorination, Bromination, and Ozonation of the Model Compound Resorcinol to THM Formation Observed in Treated Post-Clarified Samples

Chlorination, bromination, and ozonation experiments were performed on aqueous model compound (resorcinol) solutions, with and without the presence of bromide, to determine whether observed increases in brominated THMs upon ozonation were a result of the formation of precursors within the organic matter during pre-chlorination. All model compound experiments were based on the assumption that resorcinol has one potential THM reactive site (Rook 1977; Howard et al. 1984), and that three chlorine or bromine atoms could become bonded to the molecule in order to form a THM. Therefore, if 100% THM formation was achieved, at a minimum 3 moles of halogen could potentially react with 1 mole of model compound, therefore a 3:1 ratio was used in the model compound experiments. The molar ratios for the experiments were based on the carbon content of the model compound (10 µM carbon L^{-1} (0.12 mg carbon L^{-1})).

Four separate scenarios for treatment of resorcinol were tested, as shown in Figure 5-2: chlorination alone (HOCl; purple boxes), bromide addition followed by chlorination (Br^-/HOCl; orange boxes), chlorination followed by hypobromous acid addition (HOCl/HOBr; green boxes), and chlorination followed by bromide addition

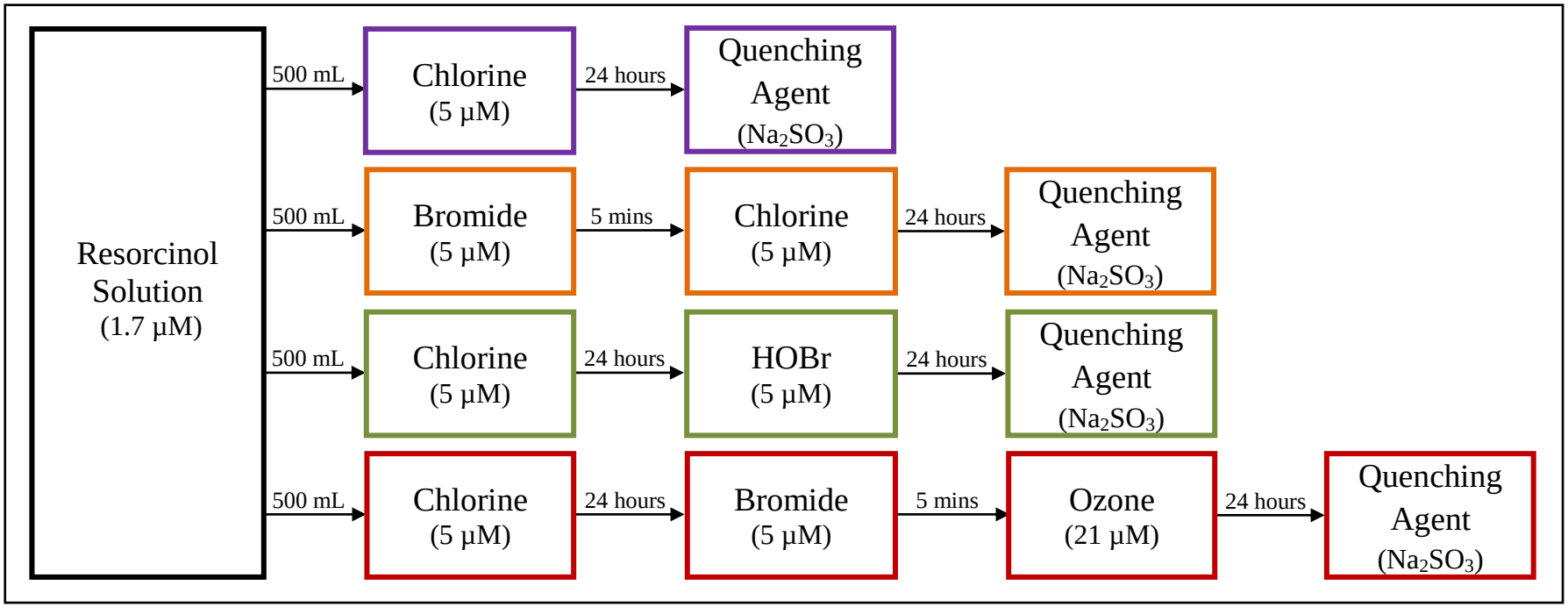


Figure 5 - 2: Schematic of the design of the treatment of resorcinol in laboratory water: 'HOCl' (purple boxes), 'Br^-/HOCl' (orange boxes), 'HOCl/HOBr' (green boxes), and 'HOCl/Br^-/O_3' (red boxes) at pH 6.5 and 7.5. The original resorcinol solution and quenched experimental solutions were analysed for THM4 and bromate formation

and ozonation ($HOCl/Br^-/O_3$; red boxes). Briefly, an aliquot (2 mL) of a stock solution of resorcinol in laboratory water (1.7 mM) was added into laboratory water (2 L), and the resulting solution was divided between two experiments (500 mL for pH 6.5 and 7.5).

Appropriate aliquots of bromide solution (5 mM as KBr), sodium hypochlorite solution (5 mM), and HOBr solution (prepared from stock solutions of hypochlorite (3 mM as Cl_2) and bromide (3.3 mM as KBr), as described in Section 5.2.2), in order to achieve initial concentrations of 5 µM, were added to the model compound solutions, and the initial concentration of ozone was 21 µM (see Figure 5-2 for order of addition and time periods between addition of bromide and/or oxidants). Upon bromide or oxidant (HOCl, HOBr, or ozone) addition to the model compound sample, the solutions were mixed for 10 seconds, and then sub-sampled into 40 mL vials with Teflon-lined caps (duplicates for THM analysis), and 10 mL plastic test tubes with caps (for bromate analysis). All vessels were filled so that they were headspace-free, and were stored in the dark. After 1 and 24 hours, the residual oxidant in the 40 mL vials was quenched with a calculated aliquot of an aqueous sodium sulphite (Na_2SO_3) (APS Finechem) solution (21 mM) such that the quenching agent added was equivalent to 5 times the molar concentration of the initial oxidant concentration. The quenched samples were then stored at 4ºC prior to THM analysis. The 10 mL plastic tube samples did not require a quenching agent, as complete oxidation was necessary for bromate analysis.

5.3 Results and Discussion

5.3.1 Groundwater Samples

The samples used in this study were taken at the post-clarification stage from the Jandakot GWTP. The borefield and groundwater treatment plant at Jandakot are described in detail in Section 4.1.2. The water quality parameters of the groundwater PC samples are shown in Table 5-1. The water quality between the water blends on the sampling days appears to be similar. All three samples contain high bromide concentrations, however it can be seen that the DOC concentrations varied significantly. In general, these samples can be considered as high DOC, low alkalinity waters. The ammonia present in the water samples is also of interest, as it could potentially affect chlorination during the experiments. There is the potential for

chloramine to form when free chlorine is added to water containing free ammonia, thereby reducing DBP formation in the samples. It can be seen that chloramine has been formed in the PC samples, and that there is still free ammonia remaining. The iodate present in the samples would have resulted from naturally occurring iodide in the raw water reacting with chlorine during pre-clarification treatment.

Table 5 - 1: Water quality parameters of the groundwater post-clarified samples at time of sampling

Water sample		**S1**	**S2**	**S3**
DOC (mg L^{-1})		3.2	2.0	3.5
UV_{254} (cm^{-1})		0.06	0.05	0.09
Alkalinity (mg L^{-1} $CaCO_3$)		73.0	80.0	85.7
Bromide (mg L^{-1})		0.90	0.99	0.94
Temperature (ºC)		24.3	25.0	24.8
pH		6.4	6.5	6.3
Chlorine (mg L^{-1})	**Free**	<0.02	<0.02	<0.02
	Total	0.35	0.36	0.71
Monochloramine (mg L^{-1})		0.20	0.36	0.43
Free Ammonia (mg L^{-1})		0.34	0.28	0.33
Bromate (µg L^{-1})		<0.5	<0.5	<0.5
Iodate (µg L^{-1})		4.5	3.2	4.1

5.3.2 Comparison of the Kinetics of Ozonation With and Without Pre-Treatment, and the Effect on Bromate Formation

5.3.2.1 R_{ct} Values

As previously stated (Section 4.1.1), the concentrations of ozone and OH radicals need to be quantified in order to understand the formation of bromate in the system. Experiments comparing the kinetics of ozonation pre-treatments on PC water samples were performed (as outlined in 5.2.3.1), in which samples S1, S2, and S3 were given pre-chlorination treatment 24 hours prior to ozonation, and the S3 PC sample was also given chlorine-ammonia treatment immediately prior to ozonation. Although chlorine residual was not measured prior to the addition of ozone, so any co-existence of oxidants cannot be established, the rate constant for the oxidation of OCl^- with ozone is relatively small, and reactions with •OH are not important for conventional ozonation processes (von Gunten 2003a). The R_{ct} values, representing the ratio of •OH exposure to ozone exposure, for each sample were calculated

(Section 4.1.1) for the second phase of ozonation (as it was not possible to measure the extremely rapid initial phase of ozonation using the available experimental apparatus), in which the ozone decreases with first-order kinetics, and the R_{ct} remains fairly constant. These R_{ct} values are shown in Table 5-2. Since the R_{ct} values are quite similar for the three samples over the different pre-treatments, it appears that, in general, the •OH and ozone chemistry did not significantly alter between the three samples, representing the three different production volumes.

The effect of pH is clearly apparent, as it can be seen that the R_{ct} values are smaller at pH 6.5 than 7.5. This is expected, due to the higher decomposition rate of ozone at the higher pH. The effect of pre-chlorination pre-treatment, however, was very interesting. It can be seen that the 4 mg L^{-1} pre-chlorination significantly decreased the R_{ct} value compared to 2 mg L^{-1} pre-chlorination. This may be attributed to the effect of the naturally occurring ammonia in the system, which efficiently consumes lower levels of chlorine. When the ammonia was exhausted (requiring approximately 1.4 mg L^{-1} (19 µM) chlorine), chlorination lowered the R_{ct}, value indicating there had been a decrease in the rate of the •OH based oxidation processes (Buffle et al. 2004). The addition of ammonia 10 minutes after 4 mg L^{-1} pre-chlorination (Experiment 5 in Table 5-2) appears to reflect this theory, as the R_{ct} value increased compared to pre-chlorination alone, representing the further consumption of free chlorine in reaction with the added ammonia (the effect of the added ammonia was later confirmed using the Kintecus modelling program (see Section 5.3.4)).

These results are comparable to R_{ct} values observed in other similar studies. Pinkernell and von Gunten (2001) performed ozone experiments on River Seine water (DOC = 2.4 mg L^{-1}, alkalinity = 3.9 mM HCO_3^- (195 mg $CaCO_3$ L^{-1})) and found an R_{ct} value of 9 x 10^{-9} at pH 8, 4.4 x 10^{-9} at pH 7, and 2.9 x 10^{-9} at pH 6. The samples used in this study had lower alkalinity; however the R_{ct} values obtained from experiments with ozone addition alone (Experiment 1 in Table 5-2) were similar, with average R_{ct} values of 2.2 x 10^{-9} and 6.7 x 10^{-9} at pH 6.5 and 7.5, respectively.

Elovitz et al. (2000b) measured the R_{ct} values in various Swiss water sources at pH 8 and 15°C. The R_{ct} values ranged between 7 x 10^{-10}, for a groundwater with a low DOC concentration (0.7 mg L^{-1}) and a very high alkalinity (6.7 mM HCO_3^- (335

Table 5 - 2: Comparison of the second phase R_{ct} values for the PC samples after pre-treatment with chlorine (S1, S2, S3) or the chlorine-ammonia process (S3), followed by ozonation (3 mg L^{-1}), at pH 6.5 and 7.5 (as described in Section 5.2.4.1 and Figure 5-1 (red boxes)).

	Pre-treatment applied prior to ozonation	S1		S2		S3	
		6.5	7.5	6.5	7.5	6.5	7.5
(1)	0 mg L^{-1} Cl_2	2.5×10^{-9}	5.6×10^{-9}	2.1×10^{-9}	6.4×10^{-9}	2.0×10^{-9}	8.1×10^{-9}
(2)	0.5 mg L^{-1} Cl_2	2.7×10^{-9}	6.3×10^{-9}	2.7×10^{-9}	7.5×10^{-9}	-	-
(3)	2 mg L^{-1} Cl_2	3.7×10^{-9}	12.2×10^{-9}	3.4×10^{-9}	13.4×10^{-9}	8.3×10^{-9}	15.6×10^{-9}
(4)	4 mg L^{-1} Cl_2	-	-	-	-	5.1×10^{-9}	7.1×10^{-9}
(5)	4 mg L^{-1} Cl_2, 0.44 mg L^{-1} NH_3	-	-	-	-	9.7×10^{-9}	-

mg $CaCO_3$ L^{-1})) leading to enhanced ozone stabilisation, to 4.0 x 10^{-8}, for a highly eutrophic lake water with high DOC concentration (3.2 mg L^{-1}) and a moderate alkalinity (3.4 mM HCO_3^- (160 mg $CaCO_3$ L^{-1})) leading to rapid ozone decomposition (Elovitz et al. 2000b). While these waters are different from the samples used in this study, and the temperature of the reaction was much lower than that used in the present study, the R_{ct} values fall within similar ranges.

5.3.2.2 Calculation of Bromide Oxidation Attributable to •OH Reaction Pathway

There are two reaction pathways for the oxidation of bromide by ozone in aqueous solution: direct oxidation by ozone and oxidation by •OH. During the initial phase of oxidation, the •OH pathway is the main pathway, where > 40 % of the Br^- can be oxidised by •OH if the R_{ct} > 10^{-7} (Buffle et al. 2004). According to von Gunten (2003), during the second phase of oxidation in which the ozone reaction pathway dominates, 96% of Br^- can be oxidised by ozone when the $R_{ct} = 10^{-8}$.

The percentage of bromide oxidation attributed to the direct reaction between bromide and •OH (*f*) can be calculated using Equation 1 (von Gunten 2003a). The rate constant for the oxidation of bromide by ozone at ambient temperature is k_{O3} = 160 M^{-1} s^{-1} (Haag and Hoigne 1983), while oxidation by •OH is $k_{\bullet OH}$ = 1.1 x 10^9 M^{-1} s^{-1} (von Gunten and Hoigne 1996).

$$f_{(\bullet OH)} = \frac{k_{\bullet OH} R_{ct}}{k_{O_3} + k_{\bullet OH} R_{ct}} \quad (1)$$

The calculated percentage of bromide oxidation attributed to the reaction between bromide and •OH for samples S1, S2, and S3 during the second phase of the ozonation process (where R_{ct} values have been determined) are shown in Table 5-3.

It was found that during the second phase of the ozonation process, 1 – 10% of the bromide oxidation was due to reactions between Br^- and •OH. This confirms the direct ozone reaction pathway is the primary source of oxidation of bromide during the second phase of the ozonation process. Under similar conditions, the S1, S2, and S3 sample waters had a similar Br^-/•OH reaction percentage. At pH 7.5, a greater percentage of Br^- was oxidised by reactions with •OH, more than doubling the

percentage observed at pH 6.5. This is expected, as there are more •OH due to ozone decomposition at the higher pH. Interestingly, the percentage of Br^-/•OH reactions increased slightly with increasing pre-chlorination dose until 4 mg L^{-1} Cl_2, wherein the percentage decreased from that observed with 2 mg L^{-1} Cl_2.

Table 5 - 3: Comparison of the percentage of bromide oxidation attributed to the reaction between bromide and •OH during the second phase of ozonation for the PC samples after pre-treatment with chlorine (S1, S2, S3) or the chlorine-ammonia process (S3), followed by ozonation (3 mg L^{-1}), at pH 6.5 and 7.5 (as described in Section 5.2.4.1 and Figure 5-1 (red boxes)).

	Pre-treatment applied prior to ozonation	S1		S2		S3	
		6.5	7.5	6.5	7.5	6.5	7.5
(1)	0 mg L^{-1} Cl_2	1.7	3.7	1.4	4.2	1.4	5.3
(2)	0.5 mg L^{-1} Cl_2	1.8	4.2	1.8	4.9	-	-
(3)	2 mg L^{-1} Cl_2	2.5	7.7	2.3	8.5	5.4	9.7
(4)	4 mg L^{-1} Cl_2	-	-	-	-	3.4	4.7
(5)	4 mg L^{-1} Cl_2, 0.4 mg L^{-1} NH_3	-	-	-	-	6.2	-

5.3.2.3 Bromate Formation

The concentrations of bromate formed from the S1, S2, and S3 samples against the ozone exposure, during experiments with no- and 2 mg L^{-1} pre-chlorination followed by ozone addition (3 mg L^{-1}), during a 15 minute time period immediately after ozone addition at pH 6.5 and 7.5 are shown in Figures 5-3 and 5-4, respectively. Due to the bromate contamination in the chlorine stock solution used in the chlorination experiments, the bromate in the blank samples (representing this contamination) was subtracted from the bromate formation in all chlorination experiments. The fast initial phase increase in bromate formation, resulting from oxidation of bromide mainly by •OH, followed by the slower second phase bromate formation, resulting from predominantly ozone oxidation of bromide, as discussed in Section 5.3.2.3, can be seen Figures 5-3 and 5-4. The pH was found to have a significant impact on the bromate formation, with pH 6.5 resulting in bromate concentrations up to 12 µg L^{-1} compared to bromate concentrations up to 35 µg L^{-1} for pH 7.5.

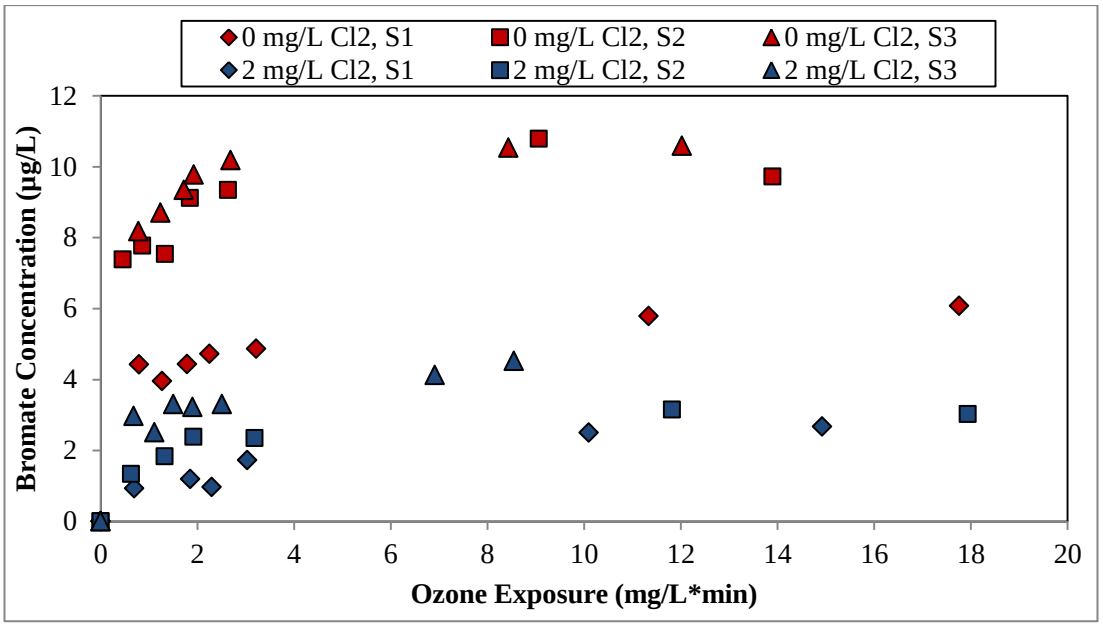


Figure 5 - 3: The concentrations of bromate formed from the S1, S2, and S3 samples against ozone exposure, after ozone addition (3 mg L^{-1}), at pH 6.5 (average ammonia concentration ~ 0.3 mg L^{-1}) (bromate concentration in the chlorine stock solution has been subtracted)

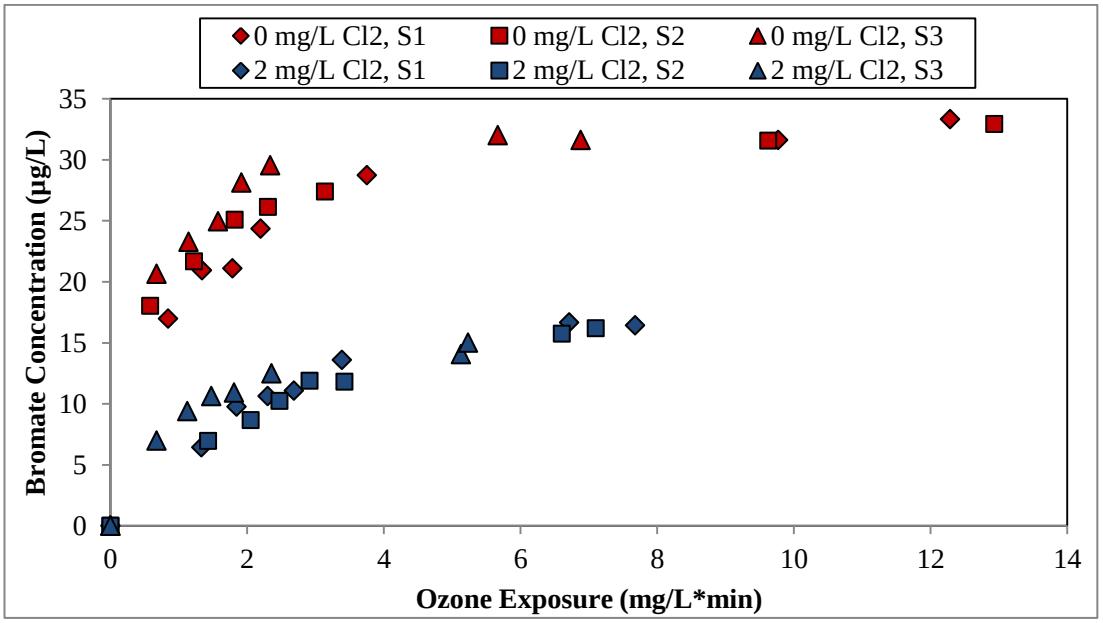


Figure 5 - 4: The concentrations of bromate formed from the S1, S2, and S3 samples against ozone exposure, after ozone addition (3 mg L^{-1}), at pH 7.5 (average ammonia concentration ~ 0.3 mg L^{-1}) (bromate concentration in the chlorine stock solution has been subtracted)

The lower bromate formation at the lower pH is consistent with the results of other studies (Krasner et al. 1993; Siddiqui and Amy 1993; Galey et al. 2000; Pinkernell and von Gunten 2001; Buffle et al. 2004). At pH 7.5, a higher •OH exposure will be observed for a given ozone exposure (higher R_{ct} values observed at pH 7.5 compared to 6.5 (Table 5-2)), resulting in higher overall oxidant exposure which leads to higher bromate concentrations.

Interestingly, Figures 5-3 and 5-4 show that the formation of bromate during the initial phase of ozonation (up to an ozone exposure of approximately 0.5 mg L^{-1} min^{-1}) decreased with pre-chlorination. It can be seen that, at both pH values, there was an approximately 40 - 50% decrease between no pre-chlorination and 2 mg L^{-1} pre-chlorination for all waters. After this initial phase of rapid bromate formation, the continuing bromate formation is more or less the same for no pre-chlorination and 2 mg L^{-1} pre-chlorination, which was unexpected, as the R_{ct} values for the second phase in the 2 mg L^{-1} pre-chlorination experiments were higher than the no pre-chlorination experiments, which should theoretically have resulted in higher bromate formation in the second phase of the 2 mg L^{-1} pre-chlorination experiments. The NOM present in the water samples also reacted with the intermediate HOBr, resulting in Br-DBPs as an additional sink for bromine (see Section 5.3.3). Bromide levels were also found to decrease with pre-chlorination, with the initial bromide concentration of the PC sample decreasing by 17 and 24% with 2 and 4 mg L^{-1} Cl_2 addition, respectively.

One possible explanation for the decrease in bromate formation with pre-chlorination treatment is that the pre-chlorination step oxidised the bromide to HOBr which reacted with the organic matter, thereby making it unavailable for further oxidation with ozone/•OH. It is also possible that the ammonia in the water reacted with the chlorine and produced HOBr to form chloramines and bromamines, thereby suppressing bromate formation upon ozonation. The latter theory was shown to be possible using the Kintecus modelling program (see Section 5.3.4).

Further investigations into the effect of pre-chlorination and the chlorine-ammonia process were performed on the S3 sample only. The S3 sample was given pre-chlorination treatment (0.5 – 4 mg L^{-1} as Cl_2) 24 hours prior to ozonation, as well as

chlorine-ammonia treatment (4 mg L^{-1} chlorine followed by 0.44 mg L^{-1} ammonia). The concentration of bromate after ozone addition (3 mg L^{-1}) at pH 6.5 and pH 7.5 is shown as a function of ozone exposure in Figure 5-5. Overall, it can be seen that similar trends are apparent for the two pH values. Chlorine-ammonia data is not included in Figure 5-5, as bromate formation was below method detection limits.

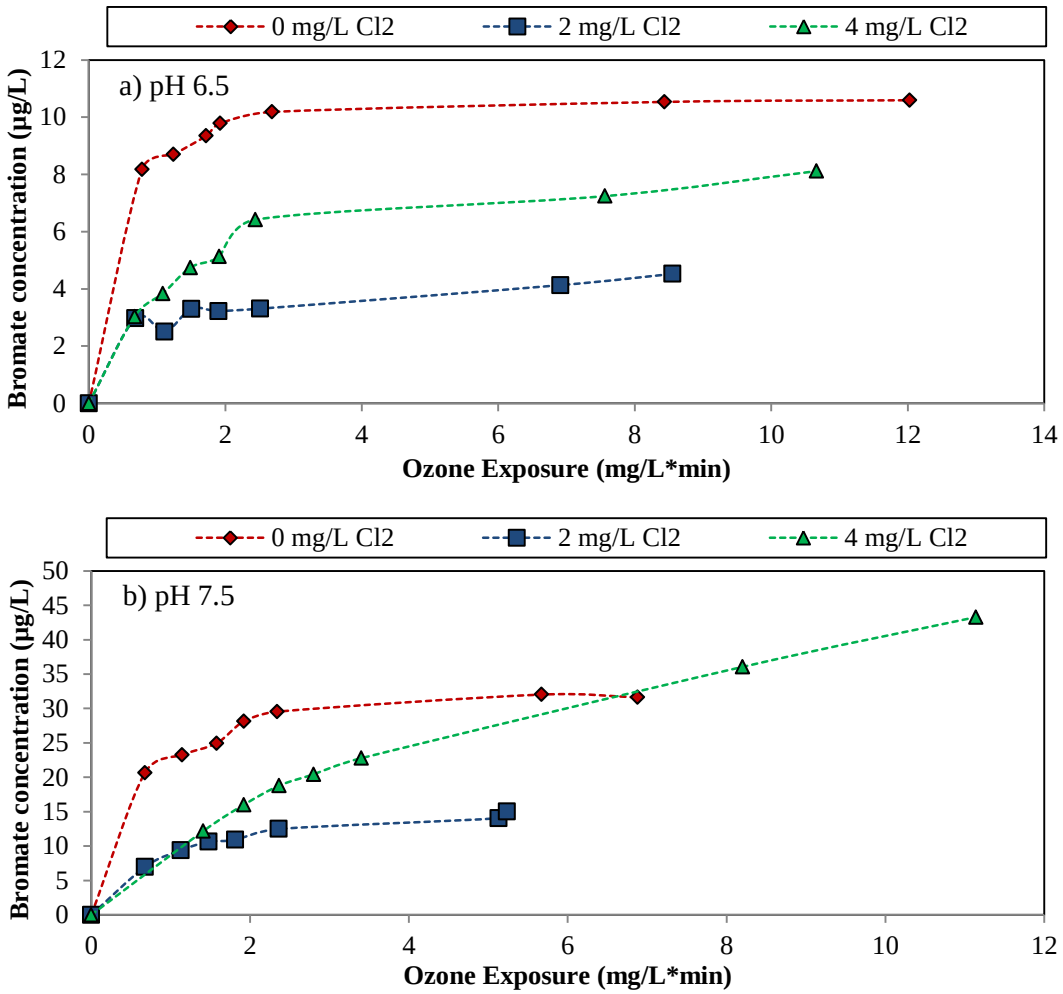


Figure 5 - 5: Bromate formation during ozonation at pH 6.5 (a) and pH 7.5 (b) [S3; 3 mg L^{-1} ozone] (bromate concentration in the chlorine stock solution has been subtracted)

The addition of chlorine prior to ozonation had a mixed effect when compared to the no pre-chlorination experiments, with 2 mg L^{-1} pre-chlorination reducing the formation of bromate at both pH values, while 4 mg L^{-1} pre-chlorination increased the bromate formation at pH 7.5 and reduced it at pH 6.5. This was an unexpected result, and it was subsequently discovered that the purchased chlorine solution used

for the experiments contained, after addition of a quenching agent, a measureable concentration of bromide, and therefore the chlorine solution contained a low concentration of HOBr. The Kintecus modelling program was used to test the effect of HOBr contamination within the experimental conditions. It was found that the presence of HOBr within the chlorine stock solution, in combination with the natural ammonia present in the sample, would significantly affect the formation of bromate during the ozonation experiments, due to the formation of chloramines and bromamines, resulting in the suppression of bromate formation upon ozonation (see Section 5.3.4).

The chlorine-ammonia process was found to significantly reduce the formation of bromate in the PC sample compared to pre-chlorination alone, as bromate levels were below detection after the chlorine-ammonia process. According to Buffle et al. (2004), the purpose of the chlorine-ammonia pre-oxidation step is to oxidise the bromide present in the water to hypobromous acid (Equation 3), which then reacts with ammonia to form monobromamine (Equation 4) and, upon ozonation, the monobromamine is slowly converted back to bromide (Equation 5), thereby reducing the bromide available for oxidation during the rapid initial phase of the ozonation process.

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \quad (2)$$

($k = 4.2 \times 10^6\ M^{-1}s^{-1}$, $pK_{aNH3} = 7$ (Choi and Valentine 2002b))

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad (3)$$

($k = 1550\ M^{-1}s^{-1}$, $pK_{aHOCl} = 7.5$ (Kumar and Margerum 1987))

$$HOBr + NH_3 \rightarrow NH_2Br + H_2O \quad (4)$$

($k = 8 \times 10^7\ M^{-1}s^{-1}$ (Haag et al. 1984), $pK_{aHOBr} = 8.8$ (Haag and Hoigne 1983))

$$NH_2Br + 3O_3 \rightarrow NO_3^- + Br^- + 3O_2 + 2H^+ \quad (5)$$

($k = 40\ M^{-1}s^{-1}$ (Haag et al. 1984))

The natural ammonia present in the sample combined with the additional ammonia added in the chlorine-ammonia process prior to ozonation resulted in the formation

of bromamine, and the successful masking of bromide during the ozonation step. This result shows the potential for the chlorine-ammonia process to be applied at the Jandakot GWTP to reduce the formation of bromate during ozonation.

5.3.3 Comparison of the Effect of the Initial Ozone Concentration, With or Without Pre- and Post-Treatment, on THM and Bromate Formation

Experiments comparing the effect of the initial ozone concentration, with or without pre- and post-treatment, on THM4 and bromate formation in PC water samples were performed (as described in 5.2.3.2 and Figure 5-1 (purple boxes)). Briefly, samples were given pre-chlorination treatment 24 hours prior to ozonation, and the S3 PC sample was also given chlorine-ammonia treatment immediately prior to ozonation. Samples were divided in two, and half were post-chlorinated 1 hour after ozonation. All samples were quenched 24 hours after ozonation/post-chlorination. The concentrations of the THM4 and bromate formed as a function of initial ozone concentration for the S2 sample with no pre-chlorination and 2 mg L^{-1} (28 µM) pre-chlorination at pH 6.5 and 7.5 are shown in Figure 5-6. As previously stated in Section 5.3.2.3, the bromate concentration in the blank samples (representing the bromate contamination in the chlorine stock solution) was subtracted from the bromate formation in all chlorination experiments.

Due to the chlorination of the raw water at the Jandakot GWTP (prior to clarification), small quantities of the THMs were already formed and were therefore present in the clarified samples taken for this investigation (concentrations of THMs for the experiments with no pre-chlorination and no ozone dose in Figure 5-6). There was a slight increase observed in the concentrations of the THMs due to chlorination of the clarified samples; however it appeared that the ozone addition had no effect on the THM formation, excluding the bromoform formation. Interestingly, an increase in the mixed Br/Cl-THMs was observed between no pre-chlorination and pre-chlorinated samples. As it is known that ozone does not produce Cl-organic compounds, the increase in Br/Cl-THMs was hypothesised to be due to an increase in the formation of halogenated THM precursors (such as R-$CHCl_2$, R-CHClBr, and R-$CHBr_2$ where R represents the rest of the organic molecule which is activated for THM formation at the halogenated carbon) within the organic matter as a result of pre-chlorination, with these precursors then ready to rapidly form Br/Cl-THMs upon

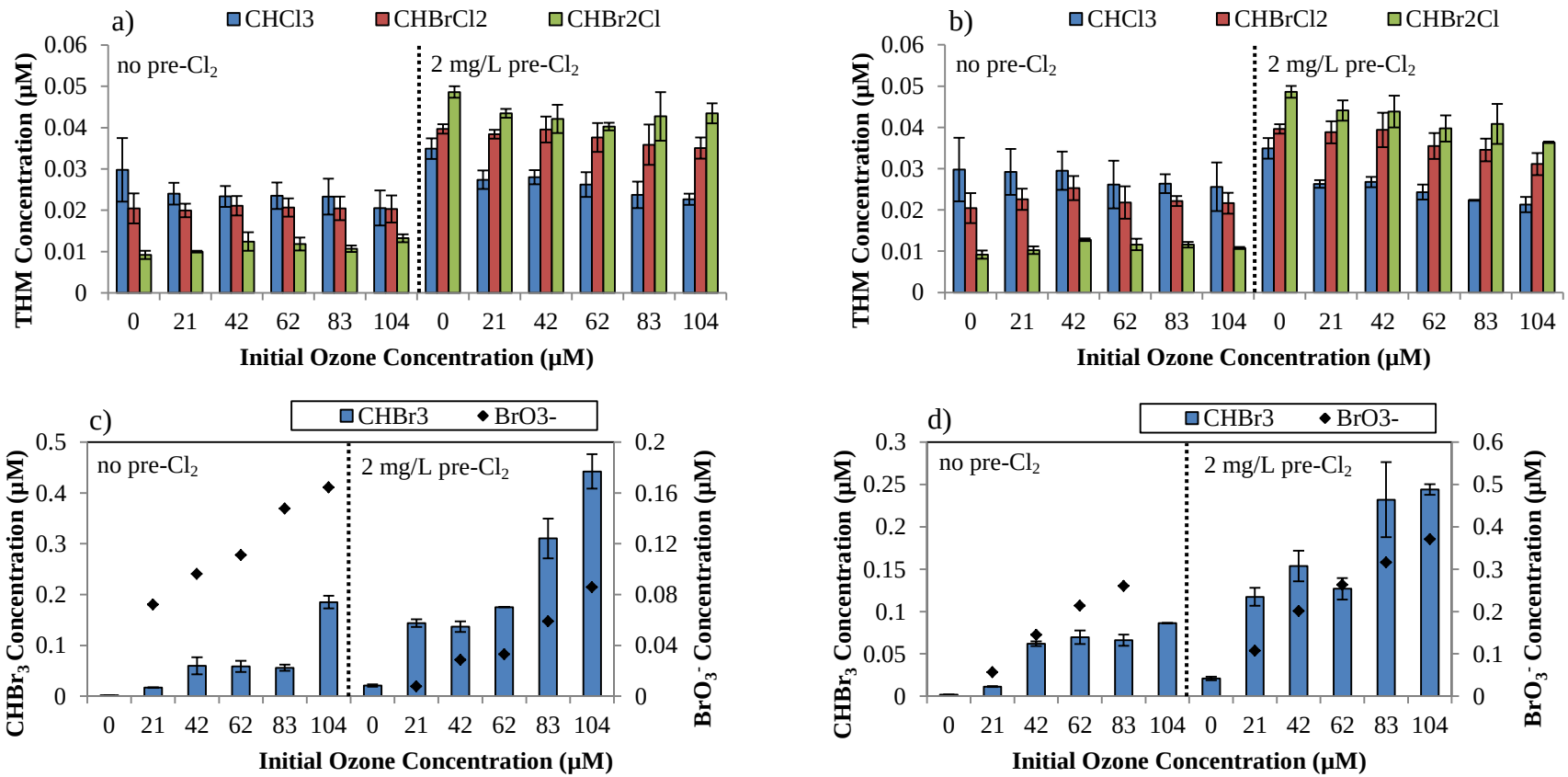


Figure 5 - 6: Concentrations of chloroform, bromodichloromethane, and dibromochloromethane as a function of initial ozone concentration at a) pH 6.5 and b) pH 7.5; concentrations of bromoform and bromate as a function of initial ozone concentration at c) pH 6.5 and d) pH 7.5. The water sample was S2 and various initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM)) were used, with no pre-chlorination and 2 mg L^{-1} (28 µM) pre-chlorination (bromate concentration in the chlorine stock solution has been subtracted)

reaction with HOBr (Equations 7 – 9) produced from the ozone-bromide reaction (Equation 6).

$$O_3 + Br^- \rightarrow HOBr + O_2 \quad (6)$$

$$R\text{-}CHCl_2 + HOBr \rightarrow R\text{-}OH + CHCl_2Br \quad (7)$$

$$R\text{-}CHClBr + HOBr \rightarrow R\text{-}OH + CHClBr_2 \quad (8)$$

$$R\text{-}CHBr_2 + HOBr \rightarrow R\text{-}OH + CHBr_3 \quad (9)$$

This hypothesis regarding the formation of halogenated THM precursors was examined using the model compound resorcinol (see Section 5.3.5).

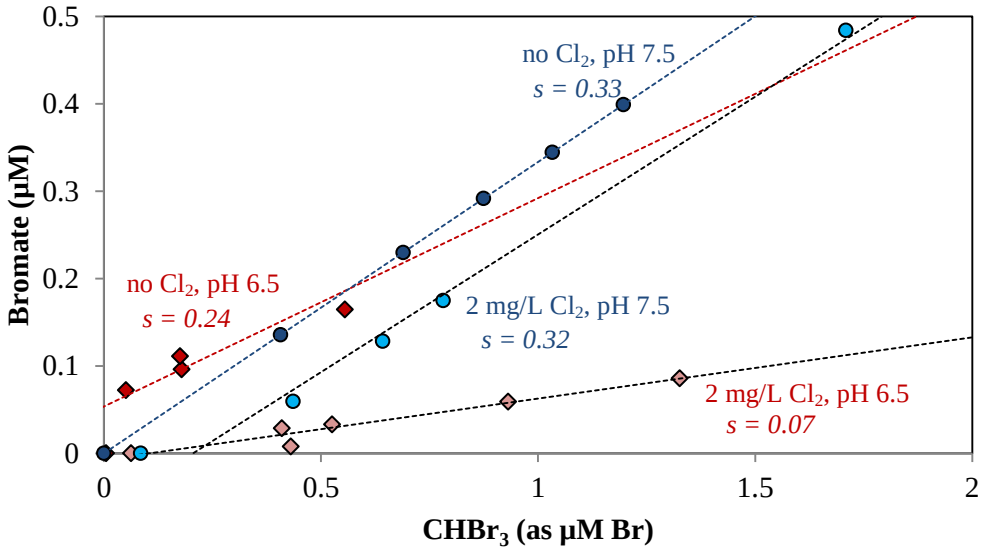


Figure 5 - 7: $CHBr_3$ vs. bromate formation from ozonation of sample S2 at pH 6.5 and 7.5; with and without pre-chlorination (2 mg L^{-1} (28 µM)) and initial ozone concentrations 0 – 5 mg L^{-1} (0 – 104 µM) (*s* = slope) (bromate concentration in the chlorine stock solution has been subtracted)

Bromoform ($CHBr_3$) was the major THM formed after ozonation, and the concentrations increased with increasing ozone dose (Figure 5-6). Figure 5-7 presents the $CHBr_3$ (as µM Br) to bromate formation for the no pre-chlorination and the 2 mg L^{-1} (28 µM) pre-chlorinated samples at pH 6.5 and 7.5 with increasing ozone dose. More Br^- was transformed into $CHBr_3$ at pH 6.5 than at pH 7.5, as shown by the lower slope value at pH 6.5. The higher R_{ct} value observed at pH 7.5,

which leads to higher •OH oxidation of HOBr to bromate, results in a smaller chance of a reaction with NOM and so lower bromoform formation. The decrease in $CHBr_3$ formation at pH 7.5, compared to 6.5, is consistent with the results of other studies. For example, Haag and Hoigne (1983) observed a decrease in bromoform formation from 15 to 5 µg L^{-1} upon ozonation (5 mg L^{-1}) of a bromide and humic acid containing solution (1 mg L^{-1} Br^-; 2 mg L^{-1} humic acid) at pH 6.1 and 8.8, respectively. Siddiqui and Amy (1993) observed decreases in bromoform formation of approximately 50 to 28 ug L^{-1} (for pH values of 6.0 and 8.5, respectively), as well as approximately 32 to 20 ug L^{-1} (for pH values of 6.0 and 8.5, respectively), for two surface waters subject to saltwater intrusion (ozone to DOC: 4 mg/mg; 1 mg L^{-1} Br^-).

The concentrations of individual THMs and bromate after ozonation treatment (0 – 5 mg L^{-1} (0 – 104 µM)) of the S3 sample with and without pre-chlorination treatment (0.5 – 4 mg L^{-1} (7 – 56 µM)), as well as chlorine-ammonia treatment (4 mg L^{-1} (56 µM) chlorine followed by 0.44 mg L^{-1} (26 µM) ammonia), at pH 6.5 are shown in Figure 5-8. The THM4 formation after post-treatment with chlorine (6 mg L^{-1} (85 µM)) from the same experiments, are shown in Figure 5-9. Data from pH 7.5 is not shown as similar trends were observed at both pH. It can be seen that the total THM formation of the Jandakot GWTP samples when pre-chlorination was followed by ozonation did not exceed the Australian Drinking Water Guidelines value of 250 µg L^{-1}. However, higher ozone doses (> 3 mg L^{-1} (62 µM)) and pre-chlorination doses (> 2 mg L^{-1} (28 µM)) resulted in bromate formation exceeding the Australian Drinking Water Guidelines value of 20 µg L^{-1} (0.16 µM). It was found that the chlorine-ammonia process also resulted in total THM formation below the Australian Drinking Water Guidelines value, and that the THM formation was similar across all of the initial ozone concentrations. The chlorine-ammonia process achieved successful suppression of bromate formation (bromate concentration < LOD), due to formation of chloramine and bromamine, thereby making bromide unavailable for bromate formation during the ozonation step.

It can be seen that there are abnormalities observed when post-chlorination was applied to the ozonated samples (Figure 5-9). It was expected that a large addition of chlorine (6 mg L^{-1} (85 µM)) would result in an increase of THMs nearing the formation potential of the groundwater blend, however it can be seen that the

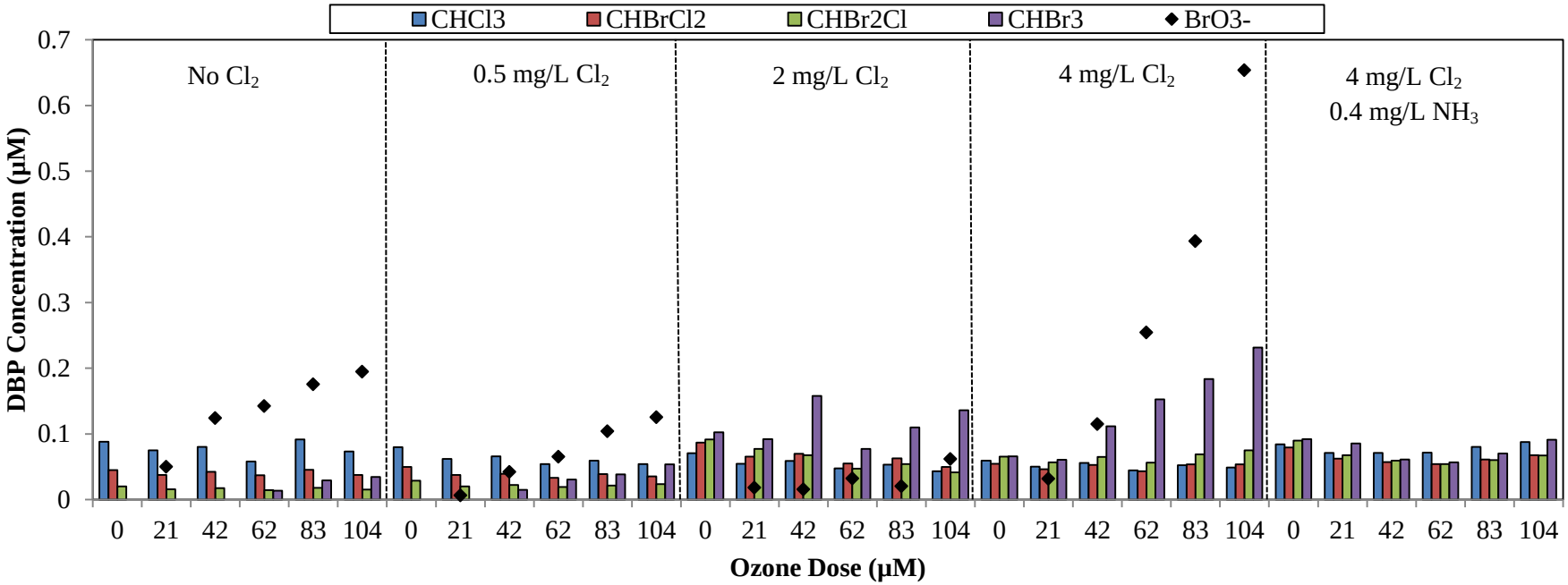


Figure 5 - 8: THM4 and bromate formation from pre-treatment (pre-chlorination or the chlorine-ammonia process) followed by ozonation of the S3 sample at pH 6.5, for various initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM)). Bromate values below the LOD were not included in the Figure (bromate concentration in the chlorine stock solution has been subtracted). Post-chlorination was not applied to these experiments

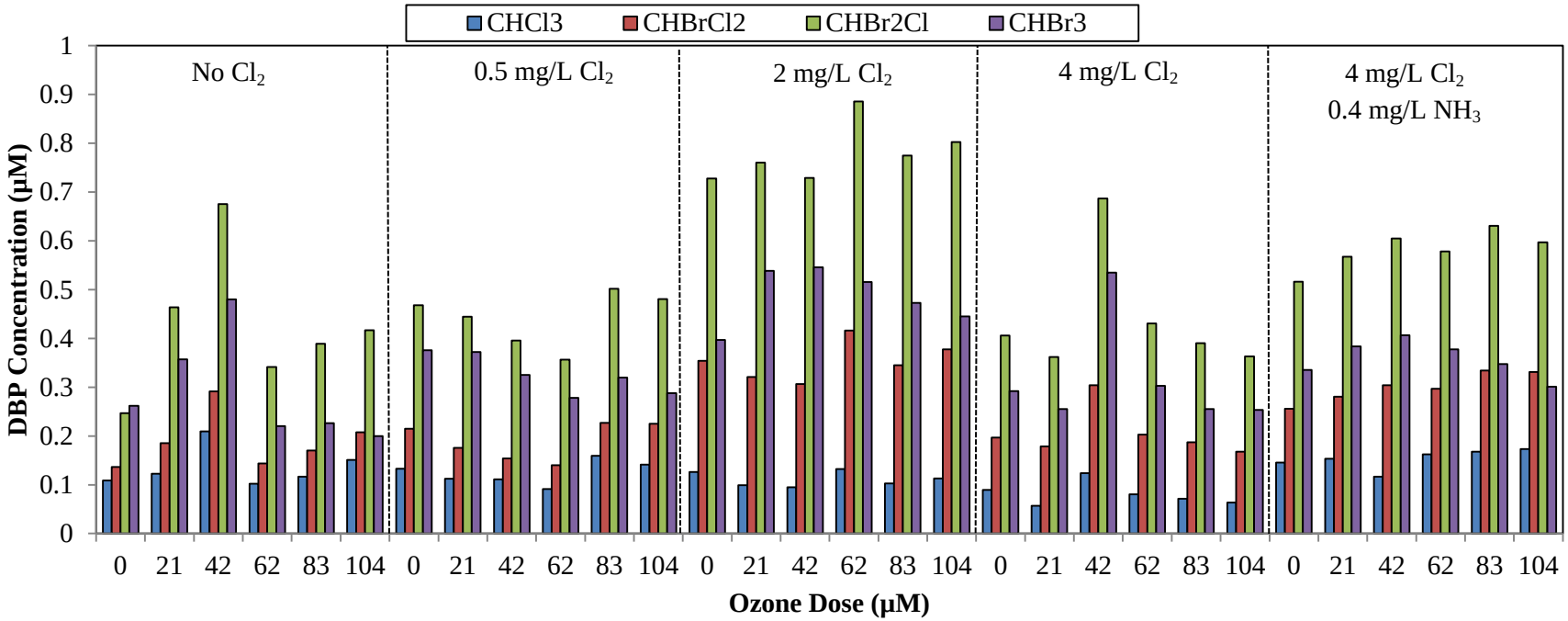


Figure 5 - 9: THM4 formation from pre-treatment (pre-chlorination or the chlorine-ammonia process) followed by ozonation of the S3 sample at pH 6.5, for various initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM)), after post-chlorination treatment (6 mg L^{-1} (85 µM)). Bromate concentrations were not included in the Figure as bromate formation is shown in Figure 5-8

resulting THM concentrations vary between the experimental parameters. In addition, the concentration of chloroform should not alter with the addition of ozone, however it was found to fluctuate between experimental conditions. The Australian Drinking Water Guidelines value for THM4 was exceeded with the addition of the post-chlorination step, however it should be noted that a BAC filtration step at the Jandakot GWTP would remove many of the THM precursors formed after ozonation, thereby reducing THM formation upon final disinfection at the plant. As expected, bromate formation did not alter with post-chlorination, and these results were therefore not included in Figure 5-9.

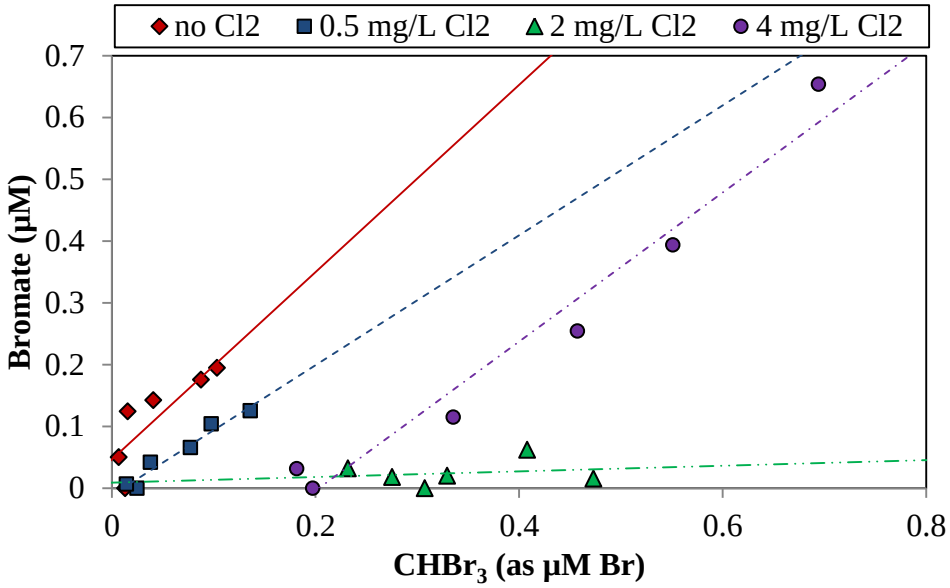


Figure 5 - 10: Bromoform ($CHBr_3$), as µM Br, and bromate formation from ozonation of the S3 sample at pH 6.5 for increasing initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM)), with and without pre-chlorination (0 – 4 mg L^{-1} (0 – 56 µM). The chlorine-ammonia process did not produce bromate levels above the LOD

Bromoform (as µM Br) and bromate concentrations from pre-treatment followed by ozonation of the S3 sample at pH 6.5, for increasing initial ozone concentrations and various pre-treatment conditions, are shown in Figure 5-10. It can be seen that both bromoform and bromate formation increased with increasing ozone dose, and that bromate generally decreased with increasing pre-chlorination dose. The exception was the 4 mg L^{-1} (56 µM) pre-chlorination experiments, where the bromate formation increased substantially. As previously hypothesised, and supported by the Kintecus modelling program (Section 5.3.4), this increase in bromate formation was likely due

to the presence of free chlorine, after exhaustion of the naturally present ammonia in the water which reacts with the chlorine and bromide to form chloramines and bromamines, thereby suppressing the bromate formation upon ozonation. In addition, as the chlorine stock solution was found to be contaminated with HOBr, the addition of a higher pre-chlorination dose, including more HOBr, was also likely to be affecting the bromate formation. This theory was tested using the Kintecus modelling program, where it was shown that the combination of ammonia concentration in the sample and HOBr contamination in the stock solution were likely to be responsible for the decrease and subsequent increase in bromate formation with increasing pre-chlorination dose (Section 5.3.4). It can also be seen that the 2 mg L^{-1} (28 µM) pre-chlorination dose resulted in a significantly different linear trend compared to the other pre-chlorination conditions. In this case, there was a considerable difference between the bromate and bromoform formation, the bromoform concentrations being higher and the bromate concentrations lower, than was observed with the 0.5 or 4 mg L^{-1} (7 and 56 µM) pre-chlorination concentrations. Figure 5-8 also shows these differences in bromate and bromoform formation, as it can be seen that the 2 mg L^{-1} (28 µM) pre-chlorination concentration resulted in significantly higher bromoform formation with lower bromate formation than the trends expected from the 0.5 and 4 mg L^{-1} (7 and 56 µM) pre-chlorination concentrations.

Figures 5-8 and 5-10 demonstrate the ‘trade-off’ between bromoform and bromate formation. Reduction in bromate formation results in a higher concentration of bromoform, due to the competing reactions between bromoform and bromate formation. As a result, a balance must be found between bromoform and bromate formation, and a possible method to minimise bromate formation whilst keeping bromoform formation low would be the chlorine-ammonia process, as shown in Figure 5-8. Therefore, further research into the potential of the chlorine-ammonia process as a pre-ozonation step would be of interest for the Jandakot GWTP.

5.3.4 Use of the Kintecus Modelling Program

In order to determine the effect of HOBr contamination in the chlorine stock solution on the bromate formation, a model in the Kintecus modelling program was prepared. The model was used to compare the resulting HOBr concentrations after pre-chlorination as an indicator of the potential bromate formation upon ozonation.

The reaction equations and rate constants used in the Kintecus model are shown in Table 5-4.

Table 5 - 4: Rate constants (M^{-1} s^{-1}) and reaction equations, as written in the Kintecus modelling program.

Rate Constant	Reaction Equation	Reference
1.58E+10 1.00E+19	HOBr==>OBr+H OBr+H==>HOBr	(Eigen and Kustin 1962)
3.16E+10 1.00E+18	HOCl==>OCl+H OCl+H==>HOCl	(Margerum et al. 1978)
3.57E+10 1.00E+12	NH3Cl==>NH2Cl+H NH2Cl+H==>NH3Cl	(Gray et al. 1978)
1550	HOCl+Br==>HOBr	(Kumar and Margerum 1987)
4.20E+06	HOCl+NH3==>NH2Cl	(Choi and Valentine 2002b)
5.00E+04	NH3Cl+Br==>NH2Br (1)	(Trofe et al. 1980)
8.00E+07	HOBr+NH3==>NH2Br (2)	(von Gunten 2003a)
2.86E+05	NH2Cl+HOBr==>NHBrCl (1)	(Gazda and Margerum 1994)
2.20E+04	NH2Cl+OBr==>NHBrCl (2)	(Gazda and Margerum 1994)

Two initial situations were set up within the model. The first (K1) contained only the initial concentration of bromide as measured in the S3 PC water sample. The second (K2) accounted for the potential contamination of the chlorine stock solution with HOBr. The initial concentrations are detailed in Table 5-5. Model parameters were set to pH 6.5, with a 24 hour time period. The resulting concentrations of bromo species obtained from the model were divided into 'Free Br' i.e. the Br still available to be transformed into bromate by ozone; and 'Quenched Br' i.e. the Br within compounds which cannot form bromate upon ozonation. The concentrations of bromo species obtained from the model are shown in Tables 5-6 and 5-7.

Table 5 - 5: Initial concentrations (µM) used in the Kintecus Model with and without contamination of HOBr in the chlorine stock solution

	No Contamination (K1)					Contamination (K2)				
Pre-Treatment	0	0.5	2	4	4(NH_3)	0	0.5	2	4	4(NH_3)
Cl_2	0	7	28	56	56	0	7	28	56	56
NH_3	19	19	19	19	38	19	19	19	19	38
Br^-	11	11	11	11	11	11	11	11	11	11
HOBr	0	0	0	0	0	0	4	15	30	30

Table 5 - 6: Concentrations of K1 species (M) at pH 6.5

Pre-Treatment		0	0.5	2	4	4(NH_3)
'Free' Br^-	Br^-	1.11E-05	1.08E-05	1.83E-06	1.00E-55	1.00E-55
	HOBr	-	-	-	-	-
	total	*1.11E-05*	*1.08E-05*	*1.83E-06*	*1.00E-55*	*1.00E-55*
'Quenched' Br^-	NH_2Br (1)	-	2.89E-07	7.12E-08	2.65E-10	9.19E-09
	NH_2Br (2)	-	1.89E-09	1.84E-08	1.38E-08	1.67E-08
	NHBrCl	-	1.89E-12	9.17E-06	1.11E-05	1.11E-05
	total	-	*2.90E-07*	*9.2E-06*	*1.11E-05*	*1.11E-05*
'Free' and 'Quenched' Cl^-	HOCl	-	-	7.85E-37	2.39E-05	6.62E-06
	OCl^-	-	-	7.84E-38	2.39E-06	6.61E-07
	NH_2Cl	-	4.83E-06	9.23E-06	7.01E-06	2.69E-05
	total	-	*4.83E-06*	*9.23E-06*	*3.42E-05*	*3.42E-05*

Table 5 - 7: Concentrations of K2 species (M) at pH 6.5

Pre-Treatment		0	0.5	2	4	4(NH3)
'Free' Br^-	Br^-	1.11E-05	8.87E-06	1.00E-55	1.00E-55	1.00E-55
	HOBr	-	1.00E-55	7.05E-06	2.20E-05	3.07E-06
	total	*1.11E-05*	*8.87E-06*	*7.05E-06*	*2.20E-05*	*3.07E-06*
'Quenched' Br^-	NH_2Br (1)	-	2.21E-06	1.45E-10	2.98E-12	2.51E-10
	NH_2Br (2)	-	3.75E-06	1.46E-05	1.68E-05	2.91E-05
	NHBrCl	-	2.82E-10	4.43E-06	2.18E-06	8.87E-06
	total	-	*5.97E-06*	*1.90E-05*	*1.90E-05*	*3.80E-05*
'Free' and 'Quenched' Cl^-	HOCl	-	-	1.15E-05	3.92E-05	3.31E-05
	OCl^-	-	-	1.15E-06	3.91E-06	3.31E-06
	NH_2Cl	-	4.83E-06	2.72E-53	1.00E-55	-
	total	-	*4.83E-06*	*1.27E-05*	*4.31E-05*	*3.64E-05*

It can be seen from Table 5-6 that when the chlorine concentration is below the ammonia concentration, the model predicted that all of the chlorine would react with ammonia to form chloramine and that there would be no chlorine remaining in the system to form HOBr. The chlorine would therefore be effectively quenched, and as the reaction of chloramine with Br^- is slow, there would still be Br^- available in solution after 24 hours. When the chlorine concentration is above the equivalent ammonia concentration (Table 5-7), the model predicted that there would be HOBr formation. This HOBr can be quenched by reaction with ammonia to form bromamine, however in the system, the ammonia would already have been consumed

to form chloramine, and therefore the HOBr is predicted to be stable in the solution and to increase with the initial chlorine concentration.

It can be seen that the model predicts that NH_2Br (1) (bromamine formation resulting from the reaction between chloramine and bromide) will decrease with increasing chlorination, as no Br^- will remain, while NH_2Br (2) (bromamine formation resulting from the reaction between HOBr and ammonia) will increase as more HOBr is formed. However, because the reaction of chloramine with HOBr is faster than the reaction of chloramine with Br^- (HOBr is quenched by chloramine), the overall 'Free Br^-' is predicted to decrease with increasing chlorine dose (K1 in Figure 5-11). This prediction, however, does not follow the general bromate formation pattern observed during the experiments from pre-treatment (pre-chlorination or the chlorine-ammonia process) followed by ozonation of the S3 sample at pH 6.5, for various initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM)) (Figure 5-8).

In K2, the chlorine stock solution was assumed to be contaminated with different concentrations of HOBr, and it was found that, for a chlorine to bromine ratio of approximately 2/1, the resulting predicted 'Free Br^-' (K2 in Figure 5-11) followed the general bromate formation pattern observed during the experiments from pre-treatment (pre-chlorination or the chlorine-ammonia process) followed by ozonation of the S3 sample at pH 6.5, for various initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM)) (Figure 5-8). When HOBr contamination is present in the chlorine stock solution, the ammonia in the system is consumed mainly by the HOBr initially present in the HOCl stock solution (as shown by NH_2Br (2) formation). As a result, when the initial concentration of HOBr is greater than the ammonia concentration, the 'Free Br^-' species is predicted to increase, thereby fitting with the experimental bromate data.

The predicted 'Free Br^-' and the actual bromate concentrations formed in the pre-treatment followed by ozonation of the S3 sample at pH 6.5, for various initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM)), experiments were found to have a linear correlation, as shown in Figure 5-12, where the bromate concentrations in the 5 mg L^{-1} (104 µM) initial ozone concentration at pH 6.5 are plotted against the predicted 'Free Br^-' for the same experimental conditions. This linear correlation was

observed for all of the experiments at different initial ozone concentrations, as well as at pH 7.5.

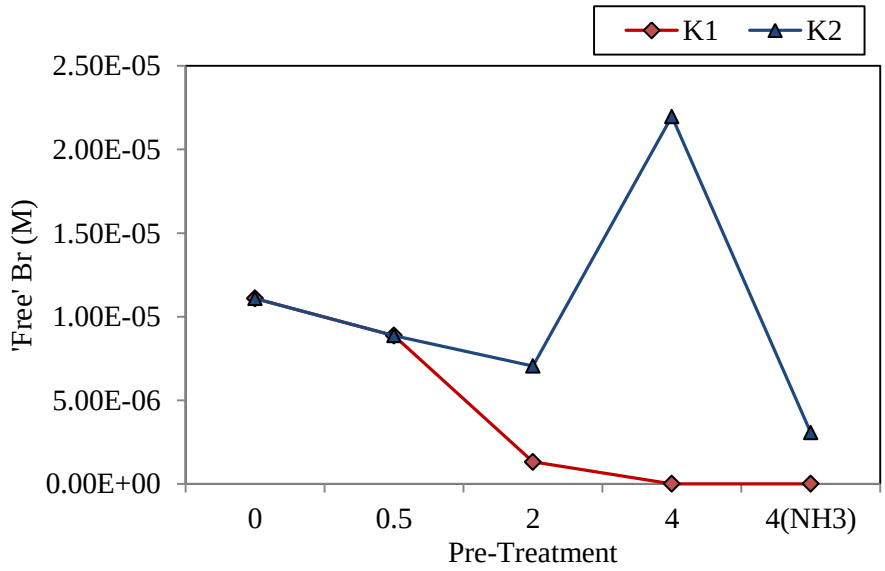


Figure 5 - 11: 'Free Br^-' predicted from the Kintecus model without HOBr contamination (K1) and with HOBr contamination (K2) for pre-treatment (pre-chlorination (0 – 4 mg L^{-1} (0 – 56 µM)) or the chlorine-ammonia process (4 mg L^{-1} (56 µM) chlorine followed by 0.44 mg L^{-1} (26 µM) ammonia)) followed by ozonation of the S3 sample at pH 6.5, for various initial ozone concentrations (0 – 5 mg L^{-1} (0 – 104 µM))

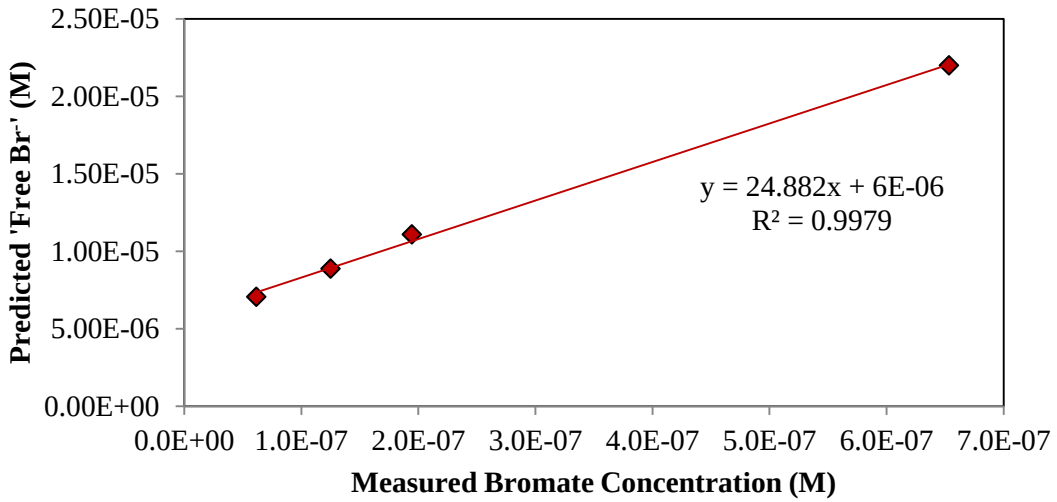


Figure 5 - 12: Predicted 'Free Br^-' against measured bromate concentration for ozonation of sample S3 with an initial ozone concentration of (5 mg L^{-1} (104 µM)) at pH 6.5

The Kintecus Modelling Program showed that the contamination of bromine in the chlorine stock solution had a significant effect on the formation of bromate as a result of pre-treatment (pre-chlorination or the chlorine-ammonia process) and ozonation. The natural ammonia present in the PC sample reacted mainly with the HOBr contamination in the chlorine stock solution, so that when the natural ammonia was exhausted, the HOBr was oxidised by ozone to form increased concentrations of bromate than would be expected (as demonstrated by the difference in bromate formation between 2 and 4 mg L^{-1} (28 and 56 µM) initial pre-chlorination concentrations). It is likely that the HOBr contamination also impacted the formation of bromo-organic compounds during pre- and post-chlorination. Therefore, care must be taken with the interpretation of the results of the Jandakot GWTP experiments.

5.3.5 Comparison of DBP Formation in Treated Post-Clarified Samples with THM and Bromate Formation from Chlorination, Bromination, and Ozonation of Solutions of the Model Compound Resorcinol

To determine whether the observed increase in brominated THMs upon ozonation was a result of the formation of precursors within the organic matter during pre-chlorination, experiments were performed using resorcinol as a model compound for NOM. The hypothesis was that pre-chlorination partially halogenated reactive sites in the organic matter, thus resulting in the ready formation of bromo-/chloro-THMs (Br-/Cl-THMs) upon further bromination by the HOBr formed during ozonation (Equations 6 – 9, Section 5.3.3). Four separate scenarios were tested on an aqueous solution of resorcinol: chlorination alone (HOCl), bromide addition followed by chlorination (Br^-/HOCl), chlorination followed by hypobromous acid addition (HOCl/HOBr), and chlorination followed by bromide addition and ozonation (HOCl/Br^-/O_3) (experimental design shown in Figure 5-2, Section 5.2.5). In each experiment, the molar equivalent concentrations of chlorine and bromide/HOBr were the same. It should also be noted that the HOCl/HOBr experiment contained a higher oxidant exposure (equal amounts of Cl_2 and pre-formed HOBr) compared to the Br^-/HOCl (Cl_2 and any HOBr formed *in situ*) and HOCl experiments.

The concentrations of individual THMs produced after 24 hours under each set of experimental conditions at pH 6.5 and 7.5 are shown in Figure 5-13. It can be seen that the THM formation was similar at both pH values. Chloroform formation was

similar between the HOCl, HOCl/HOBr, and HOCl/Br^-/O_3 experiments, while less chloroform was formed in the HOCl/Br^- experiment. This difference in chloroform formation is likely to be due to the 24 hour chlorine contact time, as the HOCl/HOBr and HOCl/Br^-/O_3 experiments both have 24 hour chlorine contact time prior to the respective HOBr or Br^-/O_3 addition, thereby allowing formation of chloroform or partially-chlorinated precursors. In comparison, the HOCl/Br^- system required HOCl to form THMs and HOBr *in situ*, resulting in lower concentrations of chloroform and halogenated-precursors.

Formation of mixed Br-Cl-THMs in the Br^-/HOCl, HOCl/HOBr, and HOCl/Br^-/O_3 experiments was of great interest. Comparison of the concentrations of mixed Br-/Cl-THMs from the Br^-/HOCl and HOCl/HOBr experiments shows that the addition of chlorine to the bromide-containing solution formed less mixed Br-/Cl-THMs than chlorination followed by bromination. It is likely that in the Br^-/HOCl system, the chlorine reacted mostly with the resorcinol before oxidising the bromide, while in the HOCl/HOBr system, chlorination resulted in the formation of additional or more reactive precursors which were then able to more readily form mixed Br-/Cl-THMs during subsequent treatment with HOBr. When ozone was applied to the system (HOCl/Br^-/O_3), the observed Br-/Cl-THMs were in smaller concentrations compared to the Br^-/HOCl and HOCl/HOBr experiments. It is likely that the lower concentration of mixed Br-/Cl-THMs in the HOCl/Br^-/O_3 system was due to the destruction of any unreacted resorcinol by ozone (Hoigne and Bader 1983a). This theory of resorcinol destruction by ozone was supported by comparison of bromoform and bromate formation as µM Br^- from resorcinol after HOCl/HOBr and HOCl/Br^-/O_3 treatment at pH 6.5 and 7.5 (Figure 5-14). It is apparent that in the HOCl/Br^-/O_3 experiments there was more bromate formation than bromoform, and that the bromoform formation was similar at the two pH values, while bromate formation was higher at pH 7.5 (as expected due to higher HOBr formation). It is therefore likely that ozone destroyed some of the unreacted resorcinol before the HOBr, formed *in situ*, could react with it, thereby decreasing the amount of HOBr consumed in the formation of bromoform from resorcinol, and instead allowing more formation of bromate from reaction of ozone with HOBr.

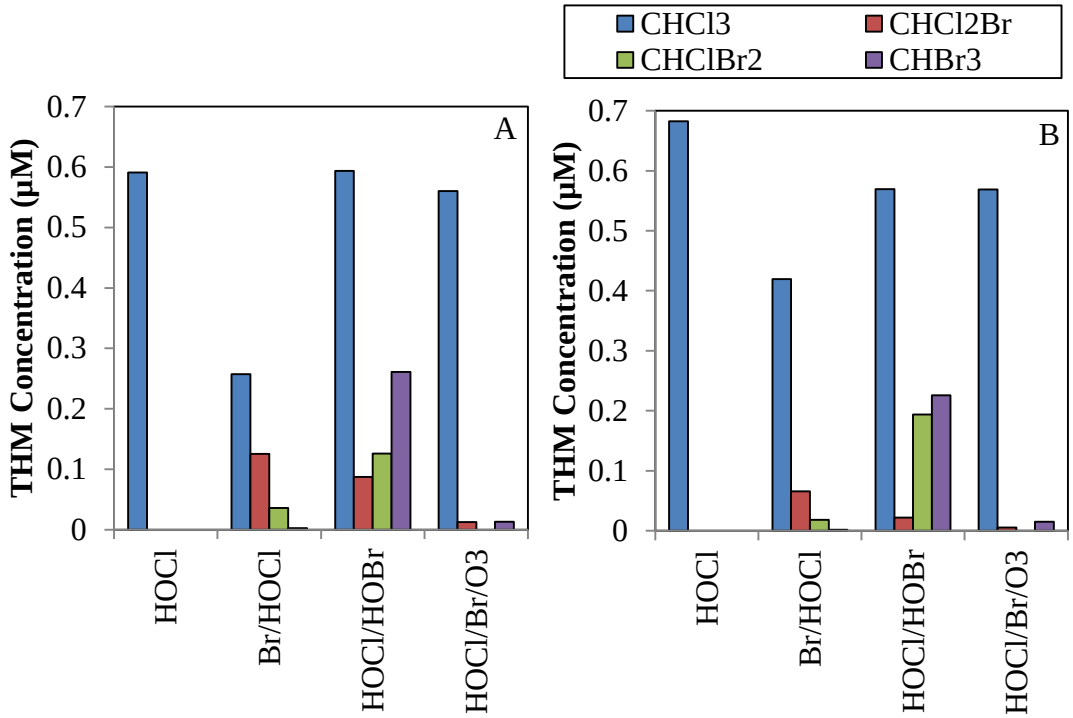


Figure 5 - 13: Concentrations of individual THMs produced after various treatments of resorcinol in aqueous solution at pH 6.5 (A) and 7.5 (B) after 24 hours

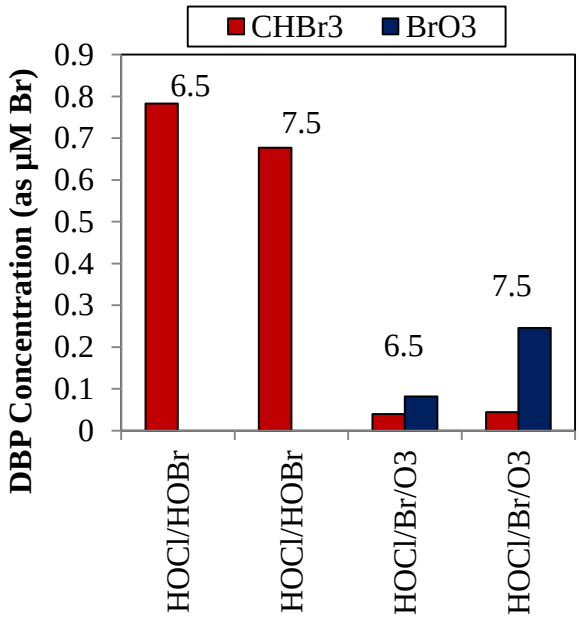


Figure 5 - 14: Concentrations of bromoform (as µM Br) and bromate produced after HOCl/HOBr and HOCl/Br^-/O_3 treatment of resorcinol in aqueous solution at pH 6.5 and 7.5 after 24 hours

The differences observed in the formation of mixed Br-/Cl-THMs in the various experiments with resorcinol support observations from the experiments with the Jandakot GWTP samples. The Jandakot GWTP PC samples were treated with various pre-treatments (chlorination and chlorine-ammonia process), and initial ozone concentrations, with or without post-treatment (chlorination) (Section 5.3.3). The mixed Br-/Cl-THMs were observed to increase during ozonation (Section 5.3.3, Figure 5-8), which could not have been a direct result of ozonation as ozonation alone does not form any Cl-organic compounds (von Gunten 2003a). Taking into account the current observations of formation of mixed Br-/Cl-THMs from resorcinol, it is likely that pre-chlorination of the Jandakot PC samples resulted in partial halogenation of organic matter in the PC samples, allowing the ready possibility of HOBr completing the reaction pathway to form THMs during ozonation, resulting in an increase in mixed Br-/Cl-THMs.

5.4 Conclusions

Comparison of the second phase R_{ct} values for each of the samples (S1, S2, and S3) showed that the ozone chemistry did not significantly alter between the different production volumes. As expected, the R_{ct} was lower at pH 6.5 than 7.5, indicating the increased stability of ozone at the lower pH. As discussed in Section 4.3.2.1, the similar R_{ct} values for the different production days and bore combinations, as well as the fact that the Jandakot GWTP had an average pH of 6.4, indicate that the ozonation process would be stable during operation, as the ozone consumption would be consistent and the lower pH value promotes ozone stability. Increased ozone stability would allow both ozone and •OH reactions to occur, potentially increasing the reduction of DBPs and their precursors.

Kinetic experiments showed that 1 – 10% of the bromide oxidation was due to oxidation of Br^- by •OH during the second phase of ozonation. Bromate formation resulted mainly from •OH reactions during the fast initial phase of ozonation, and ozone reactions during the slower second phase of ozonation.

Through experimentation using varying initial ozone concentrations, it was found that bromate formation increased with increasing initial ozone concentration. This

increase in bromate formation shows the particular challenge faced when ozone is applied to waters containing high concentrations of bromide. With the application of chlorine prior to ozonation, bromate formation decreased with increasing chlorination concentration until 4 mg L^{-1} (56 µM), wherein the bromate formation increased significantly. Using the Kintecus modelling program, it was determined that when Br^-/HOBr contamination originating from the chlorine stock solution was present, the ammonia in the system was consumed mainly by the HOBr initially present in the HOCl stock solution. As a result, when the initial concentration of HOBr was greater than the equivalent ammonia concentration, the 'free bromide' species increased, thereby resulting in increased bromate formation.

The application of the chlorine-ammonia process (4 mg L^{-1} (56 µM) Cl_2 and 0.44 mg L^{-1} (26 µM) NH_3) resulted in negligible bromate formation upon ozonation. The chlorine-ammonia process therefore has the potential to reduce bromate formation in waters containing high bromide concentrations. Further investigation into the potential use of the chlorine-ammonia process in conjunction with an ozonation step is necessary in order to ensure bromate formation below the Australian Drinking Water Guidelines value of 20 µg L^{-1} (0.16 µM).

Bromoform was generally found to increase with increasing ozone dose, as well as increasing pre-chlorination dose. The chlorine-ammonia process resulted in a slight decrease in bromoform formation compared to the 4 mg L^{-1} (56 µM) pre-chlorination. It was also observed that the mixed Br-/Cl-THMs increased with increasing pre-chlorination dose. Further investigations into the effect of chlorination prior to ozonation using the model compound resorcinol showed the observed increase in brominated THMs upon ozonation of the PC water samples was likely to be a result of formation of partially-halogenated organic THM precursors, which can then react with HOBr during ozonation to form mixed Br-/Cl-THMs. Therefore, while chlorine addition prior to ozonation can assist in the reduction of bromate formation, it can also lead to the increased formation of other undesirable DBPs. The 'trade-off' between bromoform and bromate formation was also observed, showing how reduction of bromate results in a higher concentration of bromoform, due to the competing reactions between bromoform and bromate formation. A balance must therefore be found between bromoform and bromate formation for the treatment of

waters containing high bromide concentrations. A possible method to minimise bromate formation whilst keeping bromoform formation low, would be the chlorine-ammonia process, and so further research into the potential of the chlorine-ammonia process as a pre-ozonation treatment step would be of interest for the Jandakot GWTP system.

Post-chlorination resulted in considerably higher THM formation, with significant increases in the mixed Br-/Cl-THM concentrations. This was likely due to the ozone and HOBr creating more precursor material within the organic matter, by transforming the larger organic matter into smaller, more reactive matter, resulting in THM formation upon chlorination. It should be noted that in an actual treatment plant, the ozonated water would be biologically filtered prior to final chlorination in order to remove these newly-formed precursors, thereby resulting in lower DBP formation upon final chlorination.

Chapter 6

I-THM AND IODATE FORMATION FROM A WATER CONTAINING A HIGH BROMIDE CONCENTRATION DURING MULTISTEP TREATMENT WITH CHLORINE AND OZONE

6.1 Introduction

The most commonly utilised disinfection methods for drinking water treatment include chemical disinfectants such as chlorine, chloramine, and ozone. While these methods are successful in significantly reducing the occurrence of infections by waterborne microbial pathogens, they have the unfortunate side-effect of reacting with natural organic matter (NOM), as well as bromide and iodide, to form disinfection by-products (DBPs). The first DBPs to be discovered in chlorinated drinking water were the trihalomethanes (THMs: chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$)) (Bellar et al. 1974; Rook 1974) and, due to concerns regarding their effect on human health, the total THM concentration is regulated in several countries (e.g. Australia (NRMMC-NHMRC 2011), the European Union (EU 1998), and United States (US-EPA 2001)). WHO has also set guideline values for each THM (as $\mu g\ L^{-1}$: $CHCl_3$: 200; $CHBrCl_2$: 60; $CHBr_2Cl$: 100; and $CHBr_3$: 100) (WHO 2008).

There are potentially six THMs in addition to the regulated four which are able to form in natural waters containing both bromide and iodide, known as iodo-THMs (I-THMs: dichloroiodomethane ($CHCl_2I$), dibromoiodomethane ($CHBr_2I$), bromochloroiodomethane (CHBrClI), chlorodiiodomethane ($CHClI_2$), bromodiiodomethane ($CHBrI_2$), and iodoform (CHI_3)). Several of these I-THMs have been identified in drinking water (Hansson et al. 1987; Karpel Vel Leitner et al. 1998; Cancho et al. 2000; Bichsel and von Gunten 2000a). I-THMs, in particular iodoform, are problematic due to their undesirable tastes and odours in finished waters (Hansson et al. 1987). Studies conducted due to taste and odour issues have reported the taste and odour threshold concentrations of iodoform as 0.02 and 5 $\mu g\ L^{-1}$, respectively (Hansson et al. 1987; Cancho et al. 2000). It was recently found that, in general, organic compounds which contain an iodo-group have enhanced mammalian cell cytotoxicity and genotoxicity in comparison to their brominated and chlorinated analogues (Plewa and Wagner 2004; Richardson et al. 2008). At present, there are no drinking water regulations for any iodo-organic compounds.

I-THMs are formed from the reaction of hypoiodous acid (HOI) with NOM. Oxidants, such as ozone, chlorine, and chloramine, can easily oxidise iodide to HOI, which is then able to react with NOM, thus forming iodo-DBPs. The risk of iodo-organic compound formation increases with varying disinfectants in the order: ozone < chlorine < chloramine (Bichsel and von Gunten 2000a). However, the HOI can also be further oxidised by chlorine or ozone to form iodate (IO_3^-) (Bichsel and von Gunten 1999). Compared to bromate (BrO_3^-), a DBP formed as a result of ozonation, iodate is not a genotoxic or carcinogenic hazard (Burgi et al. 2001), and can be considered to be nontoxic due its rapid reduction to I^- by glutathione once ingested (Taurog et al. 1966). The formation of iodate is therefore desired as it consumes HOI and therefore lowers the potential for formation of iodo-organic compounds.

Chloramine is unable to oxidise HOI to iodate (Bichsel and von Gunten 1999), and as a result, HOI has a longer lifetime during chloramination compared to chlorination, therefore allowing more opportunity for formation of I-THMs and other iodo-organic compounds in chloramination (Bichsel and von Gunten 2000a; Bichsel and von Gunten 2000b). Several researchers have also found an increase in I-THMs, particularly iodoform, when applying chloramine compared to chlorine (Hansson et al. 1987; Karpel Vel Leitner et al. 1998; Bichsel and von Gunten 2000a; Krasner et al. 2006). Recently, Goslan et al. (2009) and Bougeard et al. (2010) found that the levels of I-THMs after chlorination were not always lower than levels formed after chloramination, and that this trend depended upon the sample water (Goslan et al. 2009; Bougeard et al. 2010). Chlorine, as HOCl, has been shown to react slower than HOI with THM precursors, with the rate depending upon the type and concentration of NOM (Bichsel and von Gunten 2000a; Hua et al. 2006). I-THM concentrations have been typically found to increase with increasing I^- concentration (Hua et al. 2006; Goslan et al. 2009).

6.1.1 Scope of Study

The aim of the study described in this Chapter was to continue the investigation into the feasibility of the addition of an ozonation step at the Jandakot Groundwater Treatment Plant (GWTP), as discussed in Chapters 4 and 5. In Chapter 4, it was determined that the optimal location of an ozonation step within the existing

Jandakot treatment process was after the clarification process, prior to the filters. In Chapter 5, kinetic experiments were performed comparing the effect of pre-ozonation treatments, as well as experiments examining the effect of initial ozone concentration and pre-and post-treatments, on the formation of bromate and THM4 from Jandakot post-clarified (PC) samples. In this Chapter, the experiments in Chapter 5 were extended in order to determine the effect of ozonation or pre-chlorination/ozonation on the formation of I-THMs and iodate from Jandakot PC samples. The impact of pH, initial ozone and chlorine concentrations, and post-chlorination on the formation of I-THMs and iodate was studied.

6.2 Experimental

6.2.1 Water Sample

There was one sampling event in the study for this Chapter, in which a PC water sample was collected from the Jandakot GWTP. The PC water sample was collected on 31st March 2010, a day on which the Jandakot GWTP was producing approximately 40 ML per day of water (pre-clarifier chlorination = 18.7 mg L^{-1}; PC DOC = 3.21 mg L^{-1}; free NH_3 = 0.33 mg L^{-1}; Br^- = 0.94 mg L^{-1}).

Water samples were collected in 4 L amber glass bottles. Samples were immediately transported back to the laboratory and filtered (0.45 µM membrane) prior to being stored at 4ºC for up to 1 month prior to use in the experiments.

6.2.2 Solvents and Reagents

All solvents and reagents used in this work were of analytical grade purity (AR grade ≥ 99% pure) or better, with the exception of the aqueous sodium hypochlorite solution (12.5%, technical grade, Ajax Finechem). Prior to chlorination of water samples, a concentrated solution of NaOCl in laboratory water was prepared and standardised using the method detailed in Section 5.2.2. This solution contained bromine (as discussed in Sections 5.2.1, 5.3.2, 5.3.3, and 5.3.4), and this contamination was considered when analysing the experimental results in this study.

Ozone stock solutions of approximately 0.7 mM were prepared using the method detailed in Section 4.2.2.

6.2.3 Measurement of Water Quality Parameters in Water Samples

6.2.3.1 Chlorine Residual Measurements

Residual chlorine concentrations (free and total) were measured using a Hach Pocket Colorimeter (as detailed in Section 3.2.3.1).

6.2.3.2 Chloramine Residual and Ammonia Measurements

Residual chloramine and ammonia concentrations were measured using a Hach Pocket Colorimeter (as detailed in Section 3.2.3.2).

6.2.3.3 UV_{254} Absorbance and Specific Ultraviolet Absorbance at 254 nm Measurements

The UV absorbance was measured as detailed in Section 3.2.3.3.

6.2.3.4 Dissolved Organic Carbon Analysis

The DOC concentration was determined as detailed in Section 3.2.3.4.

6.2.3.5 Bromide, Bromate, and Iodate Ion Measurements

Bromide, bromate, and iodate ions were measured as detailed in Section 4.2.3.6.

6.2.3.6 **p-***Chlorobenzoic Acid Measurements*

p-Chlorobenzoic acid (pCBA) was quantified as detailed in Section 4.2.3.7.

6.2.3.7 Ozone Measurements

The concentrations of dissolved ozone in the experimental reaction solutions were determined as detailed in Section 4.2.3.8.

6.2.3.8 Solid-Phase Microextraction / Gas Chromatography-Mass Spectrometric Analysis of I-THMs

Six I-THMs (dichloroiodomethane ($CHCl_2I$), dibromoiodomethane ($CHBr_2I$), bromochloroiodomethane (CHBrClI), chlorodiiodomethane ($CHClI_2$), bromodiiodomethane ($CHBrI_2$), and iodoform (CHI_3)) were analysed via headspace solid-phase microextraction (SPME) followed by gas chromatography with mass spectrometric (GC-MS) detection according to the standard operating procedure for an existing method previously reported by Allard et al. (2012) (which was

summarised in Section 5.2.3.8). All samples were analysed in duplicate and blank samples were also analysed.

The limits of detection (LODs) were calculated for every analytical batch using the EPA Method Detection Limit method (US-EPA 2004) by using the standard deviation of replicate analyses (n = 3) of standard solutions 50, 1000, and 5000 ng L^{-1} concentration. The average LODs for $CHCl_2I$ and CHI_3 were 40 ng L^{-1} (0.19 and 0.10 nM, respectively); $CHBr_2I$ and CHBrClI were 18 ng L^{-1} (0.07 and 0.06 nM, respectively); and for $CHClI_2$ and $CHBrI_2$ were 22 ng L^{-1} (0.07 and 0.06 nM, respectively).

6.2.4 Procedures for the Various Ozonation Experiments on Post-Clarified Water Samples, Including Pre-Chlorination, Variation of Initial Ozone Concentration, and Post-Chlorination

All experiments were carried out at pH 6.5 and 7.5, and the samples were adjusted to the desired pH by adding dilute (0.1 M) aqueous hydrochloric acid or sodium hydroxide solutions.

For all experiments involving 24 hour chlorination, sodium hypochlorite solution was added to achieve the desired concentration, and the solution was kept in the dark for 24 hours.

6.2.4.1 Effect of the Initial Ozone Concentration, With and Without Pre- and Post-Treatment, on I-THM and Iodate formation

The experiments on pre- and post-treatment of the water samples with the variation of initial ozone concentrations for the comparison of I-THM and iodate formation are shown schematically in Figure 6-1. The initial experimental conditions were the same as those described in Sections 5.2.4.1 and 5.2.4.2. Briefly, the PC sample (S3) was given pre-chlorination treatment, in which it was chlorinated (0 – 4 mg L^{-1} (0 – 56 µM) as Cl_2) 24 hours prior to ozonation. Upon ozone addition, each solution was were mixed for 10 seconds, and then divided into two parts (250 mL) in order to prepare samples with and without post-treatment. Post-treatment involved the addition of chlorine (6 mg L^{-1} (85 µM) as Cl_2) 1 hour after ozone addition. These

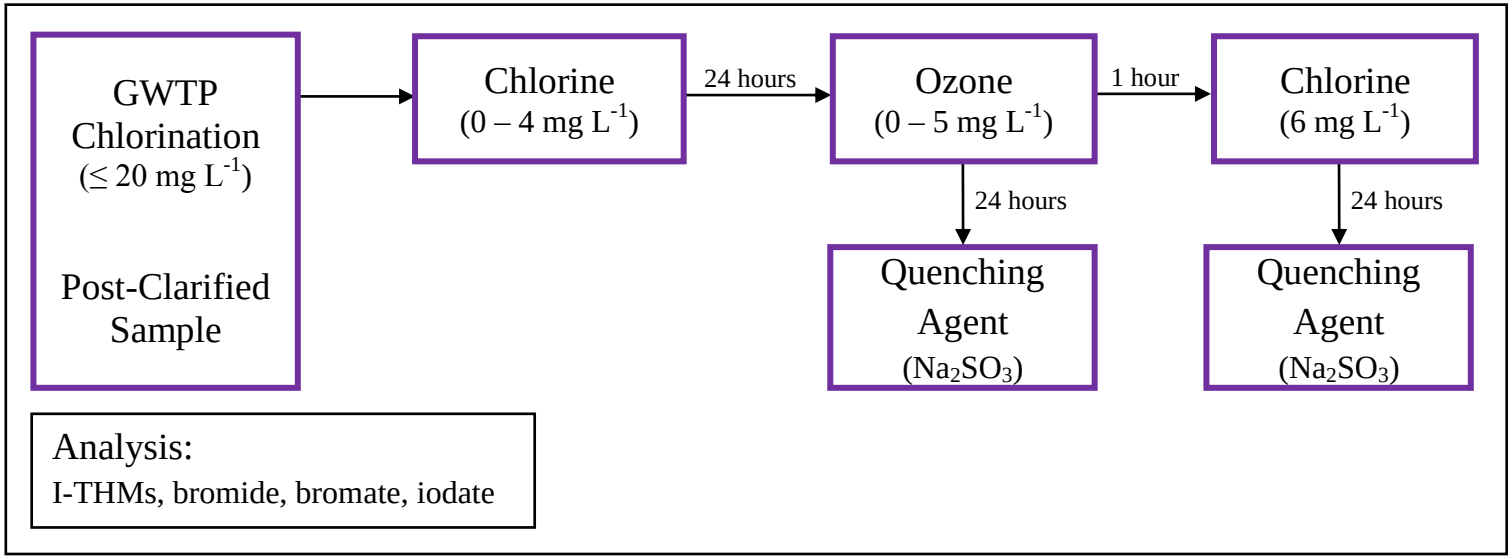


Figure 6 - 1: Schematic of the experimental design of the effect of initial ozone concentration, with and without pre- and post-treatment, on I-THM and iodate formation experiments. The pre-treatment applied to the GWTP post-clarified samples prior to the ozone (0 – 5 mg L^{-1} (0 – 104 µM)) was pre-chlorination (0 – 4 mg L^{-1} (0 – 56 µM)). The post-treatment applied to half the volume of the ozonated samples was post-chlorination (6 mg L^{-1} (85 µM))

solutions were sub-sampled into 40 mL vials with Teflon-lined caps (duplicate vials for THM analysis) for samples after pre-treatment/ozonation, as well as after post-treatment, and 10 mL plastic test tubes with caps (for bromide, bromate, and iodate analysis) for samples after pre-treatment/ozonation only. All vessels were filled so that they had no headspace, and were stored in the dark.

The residual chlorine in the 40 mL vials was quenched with a calculated aliquot of an aqueous sodium sulphite solution (21 mM) such that the quenching agent added was 5 times the molar concentration of the initial disinfectant concentration. Samples without post-treatment were quenched 24 hours after ozonation (for experimental consistency and comparison with post-treatment), while samples with post-treatment were quenched 24 hours after post-chlorination. The quenched samples were then stored at 4ºC prior to I-THM analysis. The plastic test tubes did not require a quenching agent, as the reaction ceased once the ozone had been consumed.

6.2.4.2 Comparison of the Kinetics of Ozonation on I-THMs in Post-Clarified Water Samples

All kinetic experiments were performed using the batch-type experiments detailed in Section 4.2.4.1. Briefly, batch-type ozonation experiments were performed by adding an aliquot of pCBA solution to all water samples prior to ozonation, after which small volumes of ozone stock solution were injected into the water sample in a closed bottle with a dispenser system. After specified reaction times, two sub-samples of the reaction mixture were dispensed into tubes containing indigo trisulphonate solution to quench the ozone reaction. The first tube sample was used for the analysis of ozone and pCBA, and the second tube sample was used for the analysis of bromide, bromate, and iodate. The initial ozone concentration used in all experiments was 3 mg L^{-1} (62 µM).

6.3 Results and Discussion

6.3.1 I-THM and Iodate Formation With and Without Pre-Treatment before Ozonation of Post-Clarified Water Samples, and the Effect of pH

Experiments comparing the effect of the initial ozone concentration, with and without pre- and post-treatment, on I-THM and iodate formation in PC water samples were performed. Briefly, samples were given pre-chlorination treatment 24

hours prior to ozonation. As stated in Section 5.3.2.1, the presence of any chlorine upon ozonation was disregarded. After ozonation, samples were divided in two, and half were post-chlorinated 1 hour after ozonation. All samples were quenched after 24 hours of exposure to their final oxidant. Of the six I-THMs analysed, only three were detected at quantifiable concentrations: $CHCl_2I$, CHBrClI, and $CHBr_2I$. In all experiments, the concentrations of these I-THMs were found to increase according to $CHBr_2I$ < CHBrClI < $CHCl_2I$. These observations are consistent with the observations of other researchers, who also found $CHCl_2I$ at higher levels than CHBrClI (Krasner et al. 2006; Goslan et al. 2009).

The PC sample, without ozonation or pre-treatment, contained a total I-THM concentration of 0.6 µg L^{-1} and an iodate concentration of 4 µg L^{-1} at pH 6.5, and an I-THM sum of 0.4 µg L^{-1} and an iodate concentration of 4 µg L^{-1} at pH 7.5 (see Table 6-2, chlorine 0 mg L^{-1}). The presence of iodate and these I-THMs is likely to be due to the pre-chlorination step at the GWTP, in which the high chlorine dose would have resulted in chlorine oxidising iodide through HOI to iodate, while chloramine (formed *in situ* from reaction of chlorine with natural ammonia present in the water) produced relatively low concentrations of I-THMs from the competing HOI reaction with NOM.

While the concentrations of I-THMs were slightly higher at pH 6.5 than 7.5 in the PC experiments without pre-treatment or ozonation, the differences did not appear to be significant. Comparison of the PC sample pre-treated with various initial concentrations of chlorine (no ozonation) later confirmed that the differences in I-THMs observed at the two pH values did not appear to be significant (see Section 6.3.2, Table 6-2). Iodate formation is not influenced by pH because both HOI and OI^- are rapidly oxidised by ozone (the respective rate constants are 3.6×10^4 and 1.6×10^6 $M^{-1}s^{-1}$ (Bichsel and von Gunten 1999)). The stable iodate formation with varying pH value is of significance for a water treatment process, as it would allow the pH to be altered in order to control bromate formation (as discussed in Section 5.3.2.3) without affecting the formation of iodate, and therefore not resulting in increased I-DBPs.

The total I-THM concentrations in the laboratory treated PC sample are similar to those observed during drinking water treatment by other researchers, as shown in Table 6-1. In addition, the weight ratio of I-THMs to THM4 of the S3 PC water without pre-treatment or ozonation at pH 6.5 and 7.5 (THM4 concentrations determined in Chapter 5, Section 5.3.3) was 2.6 and 1.6 %, respectively. These values are also comparable to those observed previously (Table 6-1). The formation of I-THMs is dependent on several factors, such as the type and stability of the disinfectant, iodide concentration, ammonia concentration, character and concentration of NOM, and pH (Bichsel and von Gunten 2000a). The authors in the studies presented in Table 6-1 assessed several drinking water treatment plants utilising different methods of treatment and final disinfection (e.g. chlorine, chloramine, and ozone). As a result, the reported concentrations reflect a variety of conditions.

Table 6 - 1: Previously reported I-THM concentrations in drinking water

Author	Cancho et al. (2000)	Krasner et al. (2006)	Goslan et al. (2009)	Bougeard et al. (2010)
I-THMs analysed	All six	All six	$CHCl_2I$ CHBrClI	$CHCl_2I$ CHBrClI
Median/average sum ($\mu g\ L^{-1}$)	<1	0.4	0.9	-
Maximum sum ($\mu g\ L^{-1}$)	-	19	3.7	0.73
Ratio I-THMs to THM4 (% median weight basis)	-	2	1.2	0.4

6.3.2 Effect of Pre-Chlorination, Without Ozonation, on the I-THM and Iodate Formation in Post-Clarified Water Samples

The total concentrations of the I-THMs and iodate from the PC water as sampled and after pre-treatment (chlorination) without ozonation at pH 6.5 and 7.5 are listed in Table 6-2. It should be noted, however, that the chlorine stock solution used in these experiments was found to be contaminated with bromine (see Section 5.2.2), and the presence of added bromine would therefore have had an effect on the formation of I-THMs and iodate. Unfortunately, iodide concentrations were not available for these

samples as, at the time, an analytical method with the required sensitivity and reliability was not available.

When chlorine was added to the sample, a maximum I-THM concentration of 5.6 µg L^{-1} was obtained (from a chlorine addition of 2 mg L^{-1} (28 µM)), with the maximum iodate concentration being 15.8 µg L^{-1} (from a chlorine addition of 4 mg L^{-1} (56 µM)) at pH 6.5, indicating that the PC sample still contained free iodide which was able to produce more I-THMs and iodate. However, the influence of the bromine contamination must be taken into account. In Chapter 5 it was found, using the Kintecus modelling program, that the Br^-/HOBr contamination within the chlorine stock solution, combined with the natural ammonia concentration present in the PC sample water, had a significant effect on the final bromate concentrations. It is likely that the contamination also had an effect on the I-THM and iodate concentrations. Hua et al. (2006) noted that bromine may induce the oxidation of iodide to HOI, particularly for waters containing high concentrations of bromide and iodide (Hua et al. 2006). Recently, Criquet et al. (2012) investigated the role of bromide in the formation of iodate and I-THMs during chlorination, and found that bromide (which is oxidised to HOBr), significantly enhanced the conversion of iodide to iodate. In addition, the I^- incorporation in I-THMs decreased with increasing bromide concentrations, likely due to the increased and rapid conversion of iodide to iodate (Criquet et al. 2012). It is therefore hypothesised that the concentrations of I-THMs observed during the pre-chlorination experiments in the present study may have been lower than what might have been expected if the chlorine stock solution was free of bromine contamination, since the bromine contamination may have led to an enhanced conversion of iodide to iodate.

The laboratory pre-chlorination step resulted in an increase in I-THM formation followed by a decrease in I-THM formation with increasing chlorine concentration, as shown in Figure 6-2. This trend has been observed previously: Hua et al. (2006) found that $CHCl_2I$ exhibited a maximum concentration after chlorination at 2 mg L^{-1}, and the other I-THMs reached a maximum after chlorination at 1 mg L^{-1} (Hua et al. 2006). In the present study, all the observed I-THMs reached maximum concentration in the 2 mg L^{-1} chlorine concentration experiment. It is likely the differences between the current study and that of Hua and colleagues (2006) are

related to the water quality of the samples and the different nature of the organic matter they contain. The increase in I-THM formation with increasing chlorine concentration up to ≤ 2 mg L^{-1} (28 µM) is interesting as, after such a large chlorine dose at the GWTP, it might be expected that most of the available iodide would have been oxidised by chloramine (as suggested by the presence of a chloramine residual shown in Table 4-4) to form HOI, which would then have reacted with NOM to form I-THMs or been oxidised further to iodate, in the GWTP.

Table 6 - 2: Total I-THM and iodate formation in the post-clarified water, with and without chlorine addition at pH 6.5 and 7.5 (no ozonation)

	Chlorine	Total I-THM Formation		Iodate Formation	
	mg L^{-1}	µg L^{-1}	nM	µg L^{-1}	nM
pH 6.5	0	0.6	2.6	4.0	22.7
	0.5	0.9	3.7	4.3	24.4
	2	5.6	20.0	4.5	25.6
	4	0.4	1.8	15.8	90.2
pH 7.5	0	0.4	1.7	4.0	22.5
	0.5	0.8	3.3	5.2	29.5
	2	5.4	19.6	4.2	22.9
	4	1.5	3.8	15.9	90.8

As there was still free ammonia (19 µM) present in the PC sample water, it is likely chloramine formation occurred upon pre-chlorination, thus contributing to the I-THM formation as chloramine is not capable of oxidising HOI to iodate (Bichsel and von Gunten 1999). Hansson et al. (1987) and Bichsel and von Gunten (2000a) similarly reported preferential I-THM formation during chloramination, particularly when ammonia was added prior to the chlorine. In the current study, I-THM formation increased, and iodate formation remained fairly constant, with chlorine doses ≤ 2 mg L^{-1} (28 µM), conditions where the ammonia concentration was higher than, or similar to, the chlorine concentration, indicating chloramine formation, with limited free chlorine present. With the 4 mg L^{-1} (56 µM) chlorination experiment, there was a significant increase in iodate formation since chlorine was in excess, resulting in the rapid oxidation of HOI to iodate. Higher chlorine doses would therefore limit the I-THM formation from this water, however it should be noted that increased chlorination would also likely result in more formation of other undesired DBPs, such as the classical THMs (THM4).

It is interesting that there was a significant increase in iodate formation with the 4 mg L^{-1} (56 µM) chlorine dose. In this instance, it is likely that the large chlorine dose resulted in HOI being oxidised to iodate by the chlorine rather than the HOI reacting with NOM to produce I-THMs. Hua et al (2006) also observed a similar increase in

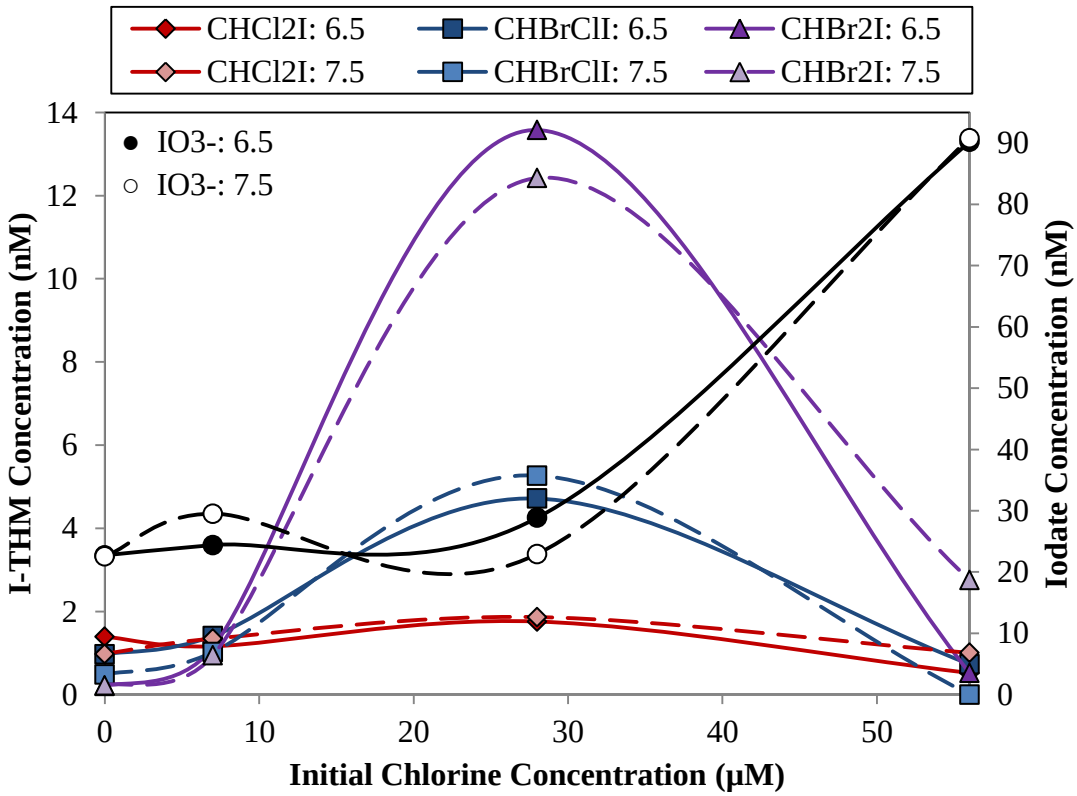


Figure 6 - 2: Effect of initial chlorine concentration on I-THM and iodate formation; in pre-chlorination (0 – 4 mg L^{-1} (0 – 56 µM)) experiments at pH 6.5 and 7.5 (no ozonation)

iodate formation in a water collected prior to treatment (DOC: 5.1 mg L^{-1}, Br^-: 63 µg L^{-1}, spiked with 2 µM iodide) when the initial chlorine concentration was increased from 0.5 to 3 mg L^{-1}, and noted approximately 86% of the initial iodide was oxidised to iodate with an initial chlorine concentration of 3 mg L^{-1}.

6.3.3 Effect of Ozonation, Without Pre-Treatment, on the I-THM and Iodate Formation in Post-Clarified Water Samples

Ozone is known to oxidise iodide to iodate, and therefore minimise the potential for I-THM formation (Bichsel and von Gunten 1999; Bichsel and von Gunten 2000a; Bichsel and von Gunten 2000b). Due to the rapid oxidation of iodide by ozone, •OH

oxidations can be disregarded in the case of iodide (von Gunten 2003a). It has been shown that when the ozone to iodide ratio is ≥ 3:1, complete oxidation (1) occurs (Bichsel and von Gunten 1999):

$$3O_3 + I^- = IO_3^- + 3O_2 \quad (1)$$

Bichsel and von Gunten (2000a) found that natural waters treated with ozone did not form detectable concentrations of I-THMs, and that > 90% of the iodide was transformed to iodate.

The concentrations of I-THMs and iodate formed from various initial ozone concentrations added to the sample water without pre-treatment with chlorine in the laboratory at pH 6.5 and 7.5 are shown in Figures 6-3 and 6-4, respectively. A significant increase in iodate formation was observed upon ozonation (even at 1 mg L^{-1} (21 µM) initial ozone concentration) and iodate formation continued to increase moderately as the initial ozone concentration was further increased. The decrease in I-THM formation relative to the increase in iodate formation demonstrates the potential for ozone to decrease I-THM formation in a water treatment process, with the ozone transforming the iodide to iodate rather than I-THMs. The similar behaviour in iodate formation between the two pH values again demonstrates the significance of the ability of a water treatment process to adjust pH for bromate control whilst still achieving beneficial iodate formation.

It is interesting to note that the concentrations of two of the detected I-THMs, $CHCl_2I$ and CHBrClI, formed in the PC water (initial ozone concentration = 0 µM in Figures 6-3 and 6-4) decreased upon ozonation with increasing initial ozone concentration, while the formation of $CHBr_2I$ remained fairly stable. A similar pattern was observed for the samples which had pre-chlorination prior to ozonation. It can therefore be surmised that ozone is not only efficient in converting iodide into iodate without forming additional I-THMs, but is also capable of destroying certain I-THMs which are already present in the water.

It is also very interesting that, at pH 7.5, $CHBr_2I$ appeared to increase with increasing ozone dose. This was unexpected, as Bichsel (2000) has previously shown that ozone

oxidises all six I-THMs. Therefore, it is possible that the chlorination of the post-clarified Jandakot sample resulted in the formation of iodinated precursors (such as R-CH_2I, where R represents the rest of the organic molecule which is activated for THM formation at the halogenated carbon) within the organic matter, which could then form $CHBr_2I$ upon reaction with HOBr produced from the ozone-bromide reaction after ozone was completely depleted. This is possible because HOBr has a longer lifetime in aqueous solutions than ozone. It should be noted, however, that in real treatment conditions, the excess HOBr would likely be quenched by a biological activated carbon (BAC) process (just as excess HOCl is known to be quenched by BAC (Chien et al. 2008)), which would be located directly after the ozonation step.

The rate constants for the reactions of the observed I-THMs with •OH were determined using the decrease of the respective I-THM after addition of 3 mg L^{-1} ozone relative to the total decrease in pCBA after the addition of 3 mg L^{-1} ozone as described in Section 6.2.4.2. The $k_{\bullet OH}$ of $CHCl_2I$ and CHBrClI were determined to be 8 (± 2) × 10^9 and 9 (± 5) × 10^9 $M^{-1}s^{-1}$, respectively. These values compare well to those reported by Bichsel (2000): 8 (± 2) × 10^9 and 7 (± 2) × 10^9 $M^{-1}s^{-1}$, respectively. It was not possible to measure the rate constant for reaction of $CHBr_2I$ with •OH in the present study due to the simultaneous formation and degradation of the compound, resulting in an increase in concentration rather than the expected decrease.

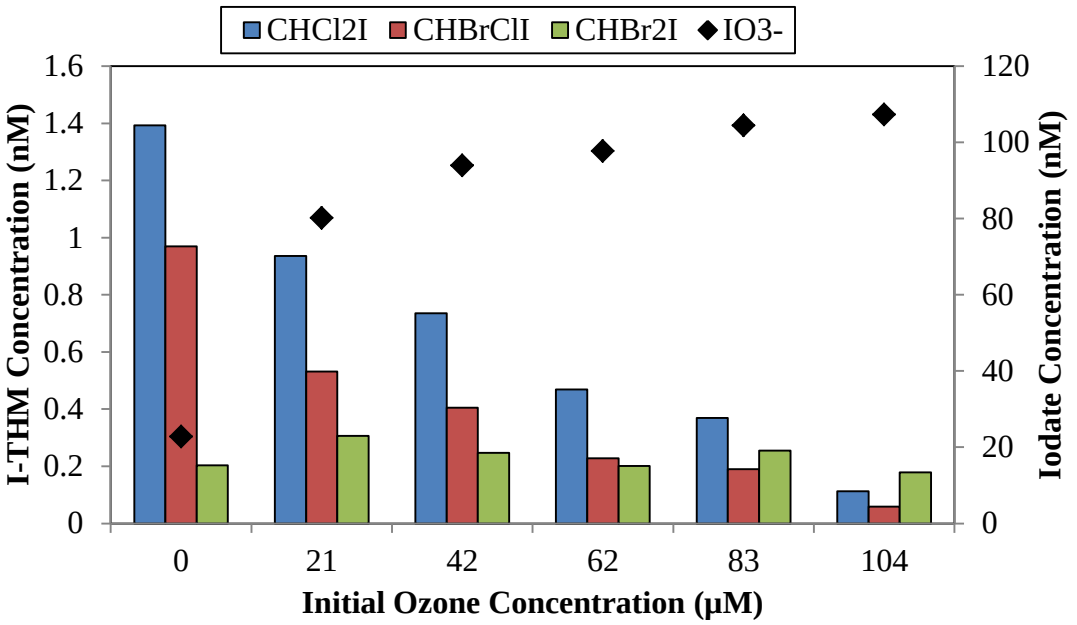


Figure 6 - 3: Concentrations of I-THMs and iodate formed from PC water (without laboratory pre-treatment) after ozonation at various initial ozone concentrations at pH 6.5

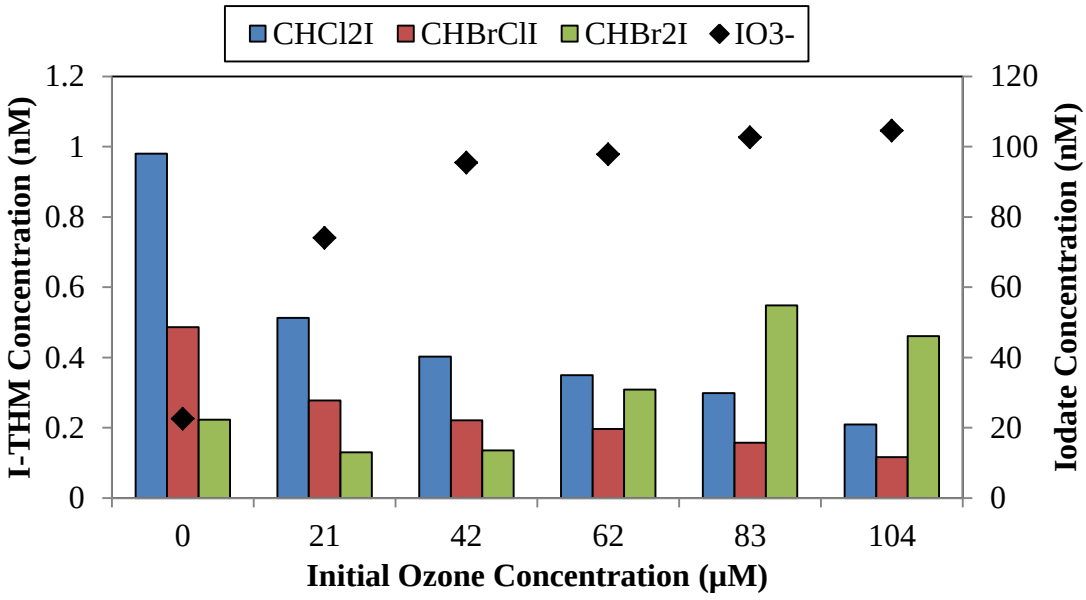


Figure 6 - 4: Concentrations of I-THMs and iodate formed from PC water (without laboratory pre-treatment) after ozonation at various initial ozone concentrations at pH 7.5

6.3.4 Effect of Post-Treatment, With and Without Pre-Treatment and Ozonation, on the I-THM and Iodate Formation in Post-Clarified Water Samples

The impact of post-treatment (chlorination) on I-THM and iodate formation was investigated. The effect of pre-treatment (initial chlorine concentration), as well as post-treatment (post-chlorination (6)), on I-THM formation (no ozonation) is shown in Figure 6-5. While pre-chlorination was found to increase and then decrease the I-THM formation, post-chlorination was found to have the opposite effect. The I-THMs initially decreased, reaching their lowest concentration at 2 mg L^{-1} (28 µM) initial chlorine concentration, before increasing again when the initial chlorine concentration was 4 mg L^{-1} (56 µM).

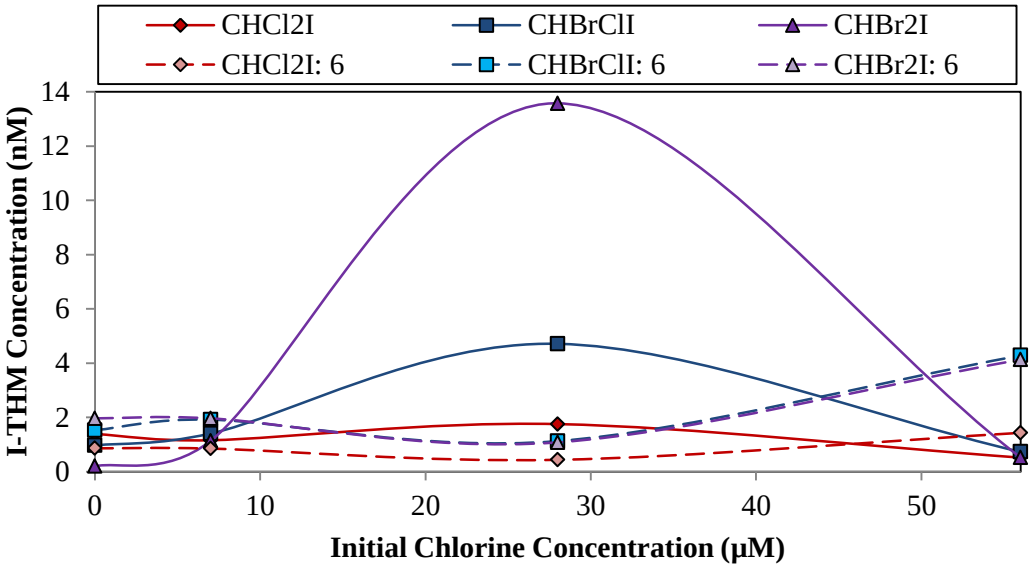


Figure 6 - 5: The concentrations of I-THMs formed from pre-chlorination (0 – 4 mg L^{-1} (0 – 56 µM)) with and without post-chlorination (6 mg L^{-1} (85 µM) chlorine; post-chlorination indicated in data legend by '6') of PC water (no ozonation) at pH 6.5.

The percentage increase in iodate concentration in the PC water after post-chlorination at pH 6.5, as compared to before post-chlorination, is shown in Table 6-3. It can be seen that post-chlorination significantly increased iodate formation when no ozone had been added to the system, likely due to the large final chlorine dose being efficient in converting I^- to iodate, though there was some additional I-THM formation. With the inclusion of ozonation prior to final disinfection, it can be

seen that the final disinfection stage resulted in less additional iodate formation. This is likely to be due to ozonation converting the majority of the I^- to iodate prior to the final chlorine addition, thus resulting in minor conversion of the remaining HOI to iodate by chlorine.

Table 6 - 3: Percentage (%) increase in iodate formation after final disinfection (with 6 mg L^{-1} chlorine; post-chlorination) at pH 6.5, compared to before final disinfection.

Initial Ozone Concentration (mg L^{-1})	Initial Chlorine Concentration (mg L^{-1})			
	0	**0.5**	**2**	**4**
0	78	76	71	61
1	31	42	39	13
2	21	29	22	7
3	17	30	14	7
4	15	19	18	3
5	10	22	11	4

6.4 Conclusions

Of the six I-THMs analysed, only three were found in detectable concentrations in the Jandakot post-clarified water. The concentrations of these I-THMs were found to increase according to $CHBr_2I$ < $CHBrClI$ < $CHCl_2I$. A change in pH of 6.5 to 7.5 did not appear to have significant influence on I-THM or iodate formation.

Laboratory pre-treatment (chlorination) was found to have a significant effect on I-THM and iodate formation. The ammonia present in the sample was likely to have formed chloramine upon chlorination, as chlorine doses ≤ 2 mg L^{-1} (i.e. ≤ the equivalent ammonia concentration) resulted in increasing I-THM formation with similar iodate formation. Chloramine does not oxidise HOI to iodate, thereby allowing HOI to react with NOM and form I-THMs. When the higher chlorine concentration (4 mg L^{-1} (56 µM)) was used, the I-THM formation significantly decreased and iodate formation increased, indicating the presence of free chlorine, which oxidises HOI to iodate. In terms of water treatment processes, chlorine addition could be used to control I-THM formation; however there is the real risk of increasing the formation of other undesirable DBPs.

Ozonation was found to significantly increase iodate formation, and •OH was found to oxidise, and hence remove, two of the three detected I-THMs ($CHCl_2I$ and CHBrClI). Ozonation may therefore be a possible solution for controlling I-THMs, and related taste and odour issues, as well as the formation of potentially toxic organic I-DBPs, in iodide-containing waters. Interestingly, however, at the higher pH, the formation and persistence of HOBr in solution was found to increase the concentration of $CHBr_2I$. Further investigation into the formation of this I-THM should be considered, and the conditions required which lead to its increase should be considered.

Final disinfection (pre-chlorine initial concentration < 4 mg L^{-1}; post-chlorine concentration 6 mg L^{-1}) was found to increase iodate formation and decrease I-THM formation. This indicates final disinfection with chlorine may also be used to control I-THM formation.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

Upon completion, the portable and flexible advanced oxidation processes (AOPs) water treatment rig will allow the treatment of water samples using various oxidation and AOP methods. The ability for the rig to be taken on site will allow real samples to be assessed, without the possibility of degradation or alteration of the sample caused by the transport and storage of large quantities of sample which is traditionally required for laboratory-based experiments. The capability of the different oxidation and AOP processes to transform DBP precursors into non-precursor material in Western Australian waters will be able to be evaluated via analysis of the DOC concentration in the raw and treated samples, as well as the reactivity with chlorine or chloramine and the subsequent DBP formation. The DOC character of the raw waters and treated samples taken from the rig will be able to be assessed using techniques such as size exclusion chromatography with UV and organic carbon detection. The information gained from the use of the water treatment rig will be used to develop optimal treatment processes to minimize DBP formation from disinfection of Western Australian waters.

The laboratory-scale study of the chlorination and chloramination of a Western Australian surface water showed that chloramination produced significantly lower concentrations of THMs, HAAs, and HANs than chlorine. The importance of regular DBP monitoring within a distribution system was emphasized as the total THM4 formation after 7 day laboratory chlorination was found to exceed the Australian Drinking Water Guidelines 250 µg L^{-1} value. As the source water is not treated for NOM removal prior to disinfection, there is the possibility of occasional THM formation over the guideline value within the distribution system. To lower DBP formation, further treatment prior to disinfection or lower doses of disinfectant, without compromising the disinfection process, should be considered for the system. Methods for reduction of the concentration of already-formed THMs in the distribution network could also be useful. Regular source monitoring to enhance understanding of how DBP formation varies over the course of the year is also recommended in order to improve management of DBP formation in this system.

Of the eight *N*-nitrosamines analysed, both chlorination and chloramination of this surface water resulted in trace NDMA and NDEA formation. Neither disinfectant resulted in NDMA formation over the Australian Drinking Water Guidelines 100

ng L^{-1} value, or even the California notification value of 10 ng L^{-1}. Interestingly, the total formation potential of NDMA and NDEA significantly increased with the higher chloramine concentration, while the higher chlorine concentration did not have significant impact on the *N*-nitrosamine concentrations.

Investigation into the addition of an ozonation step at the Jandakot GWTP showed that the clarification process stabilised the waters, rendering the different bore combinations to be of similar quality. The quality of the water post-clarification compared to the raw water was such that the performance of ozone would be significantly improved in the post-clarification water. It was found that the raw water sample had a significantly higher R_{ct} value (representing the ratio of •OH exposure to ozone exposure, as measured by the decrease in pCBA concentration), compared to the post-clarified (PC) and post-filtered (PF) samples, and required double the ozone dose of the treated samples (PC and PF) in order to allow sufficient time for kinetic analysis of the decay of ozone, unless the DOC character of the Raw water was first altered by chlorination. Comparison of the R_{ct} values between PC water on three different sampling days also showed that the clarification process stabilised the waters, rendering them to be of similar quality. It was therefore determined that an ozonation step would be best located between the clarification process and filtration, as the required ozone dose would be lower than for the raw water, due to the significant amount of NOM removed during coagulation, providing a more economical option. A conversion of the existing filtration stage into a biological filtration step following ozonation would potentially remove biodegradable organic ozonation products, which would result in increased water quality and a decrease in DBP formation upon chlorination for disinfection.

The R_{ct} of the PC sample was lower at pH 6.5 than 7.5, signifying the increased stability of ozone at the lower pH. The average pH of the Jandakot GWTP water in the current study was 6.4, indicating that the GWTP already operates at a pH suitable for an ozonation process. However, alteration in the pH or water quality could result in bromate concentrations above the Australian guideline value of 20 µg L^{-1}. Bromate formation was found to increase with increasing initial ozone concentration, and resulted mainly from •OH reactions during the fast initial phase of ozonation, as well as ozone reactions during the slower second phase of ozonation. Kinetic

experiments showed that 1 – 10% of the bromide oxidation was due to oxidation of Br^- by •OH during the second phase of ozonation.

When a pre-chlorination dose was applied prior to ozonation, bromate formation decreased with increasing chlorination dose until 4 mg L^{-1}, wherein the bromate formation increased significantly. The application of the chlorine-ammonia process (4 mg L^{-1} Cl_2 and 0.4 mg L^{-1} NH_3) resulted in negligible bromate formation upon ozonation. Using the Kintecus modelling program, it was found that when HOBr contamination was present in the chlorine stock solution, the ammonia in the system was consumed mainly by the HOBr initially present in the HOCl stock solution. As a result, when the initial concentration of HOBr was higher than the ammonia concentration, the 'free bromide' species increased, thereby resulting in increased bromate formation. Bromoform was generally found to increase with increasing ozone dose, as well as increasing pre-chlorination dose, while the mixed bromo-/chloro-THMs (Br-/Cl-THMs) also increased with increasing pre-chlorination dose. Investigations using the model compound resorcinol showed the observed increase in mixed Br-/Cl-THMs was likely to be a result of the formation of partially-halogenated organic THM precursors, which could then react with HOBr during ozonation to form mixed Br-/Cl-THMs. Despite the interference of the contaminated chlorine, it was shown that a decrease in bromate formation resulted in an increase in bromoform formation, demonstrating that optimisation of the process would be required to find an appropriate balance between bromate and bromoform formation in order to comply with their respective guideline values.

Three of the six analysed I-THMs were found in the Jandakot PC water, and the concentrations increased according to $CHBr_2I$ < $CHBrClI$ < $CHCl_2I$. pH did not appear to have a significant influence on I-THM or iodate formation. Ozonation of the PC sample significantly increased iodate formation, and two of the three detected I-THMs ($CHCl_2I$ and $CHBrClI$) were observed to decrease with increasing initial ozone concentration. This indicates ozone may be a possible solution for controlling I-THMs in I^- containing waters, as ozone has the potential to degrade I-THMs. Interestingly, however, at pH 7.5, the increase in HOBr concentration, as well as its persistence in solution, was found to increase the concentration of $CHBr_2I$. Further investigation into the observed increase in $CHBr_2I$ is recommended, as ozonation is

expected to decrease, rather than increase, the I-THM concentrations, and the conditions which result in an increase in the I-THMs should be determined.

Pre-chlorination was found to have a significant effect on I-THM and iodate formation in the PC water, without ozonation. The bromine contamination in the chlorine stock solution likely had a significant effect on the I-THM and iodate concentrations, as it has been reported that the presence of bromide increases the rate of conversion of HOI to iodate. Despite this contamination, initial chlorine concentrations $\leq$ 2 mg L^{-1} (i.e. $\leq$ equivalent ammonia concentration) resulted in chloramine formation, thereby increasing I-THM formation, with similar iodate formation, while in comparison, when the higher chlorine concentration (4 mg L^{-1}) was used, the I-THM formation significantly decreased and iodate formation increased, indicating the presence of free chlorine. It can therefore be concluded that chlorine has the potential to be used to control I-THM formation; however, there is the risk of increasing the formation of other undesirable DBPs.

Post-chlorination of the ozonated PC sample resulted in considerably higher THM formation, compared to no post-chlorination, with significant increases in the mixed Br-/Cl-THM concentrations. This increase may be due to the formation of more THM precursor material within the organic matter by reaction with ozone and HOBr, resulting in more THM formation upon chlorination. However, if ozonation was implemented in a treatment plant, the ozonated water would be bio-filtered prior to final chlorination, most likely removing these newly-formed THM precursors. Iodate formation was observed to increase with post-chlorination, and I-THM formation decreased, indicating post-chlorination may also be used to minimise I-THM formation.

This Thesis focused on the formation of regulated DBPs (THM4, HAAs, and bromate) and emerging DBPs (*N*-nitrosamines, HANs, and I-THMs) under conditions relevant to those faced by the Western Australian water industry. The laboratory-scale experiments which were performed enabled the study of DBP formation under a variety of conditions, and several sub-topics were studied, including reaction of DBP precursors (NOM, bromide, and iodide ions), impact of type of disinfectant used (chlorine and chloramine), reactions of ozone as an oxidant,

and the effect of pH. The formation of *N*-nitrosamines in the surface water was of particular interest, as *N*-nitrosamines other than NDMA had not previously been studied in Australian drinking waters. This project has also furthered the understanding of the potential for ozone to be used as an oxidant during drinking water treatment, which could not only greatly enhance the treatment of groundwater high in bromide concentration at the Jandakot GWTP, but the treatment of other drinking water sources in the broader Australian and international community.

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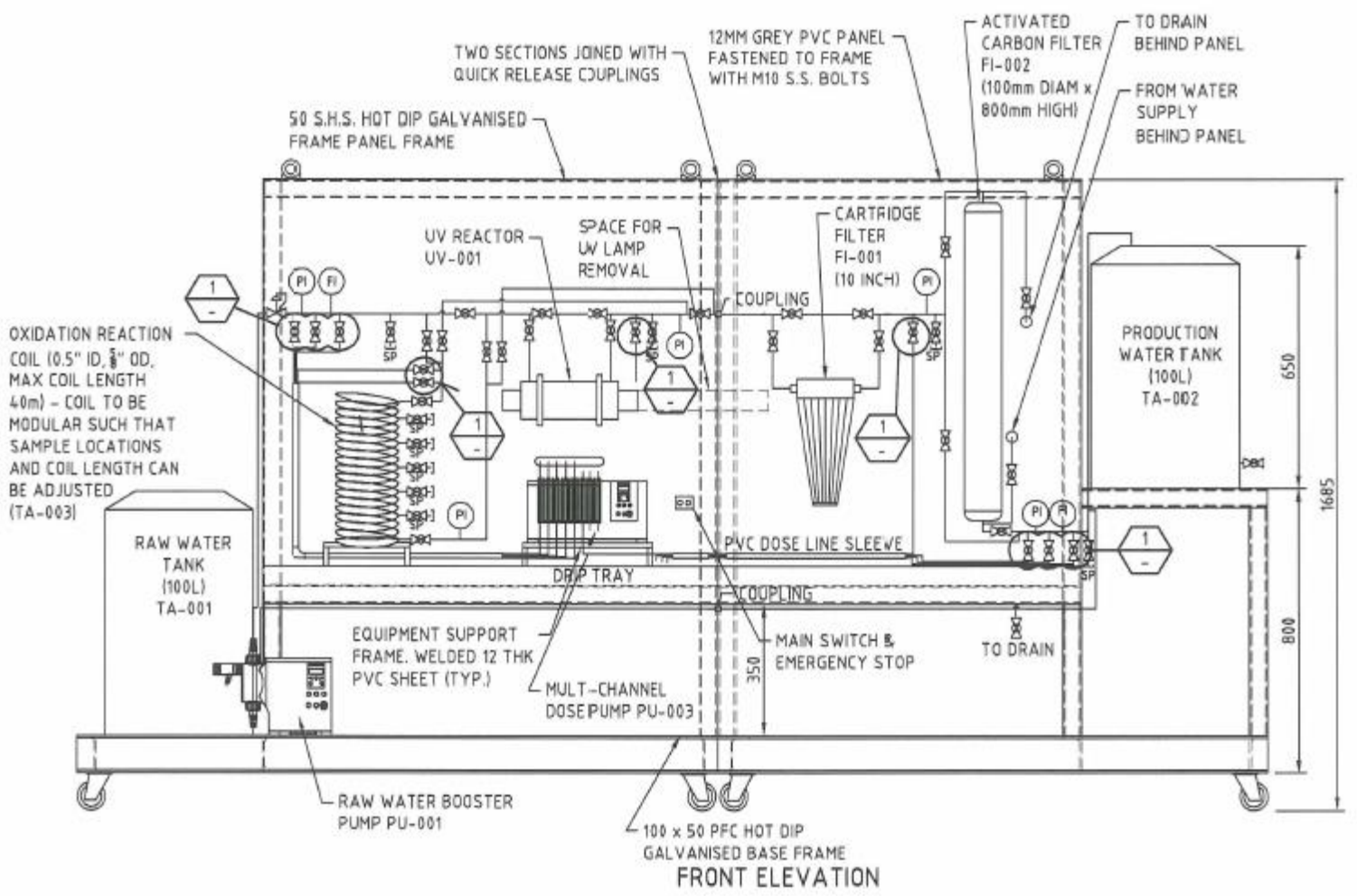
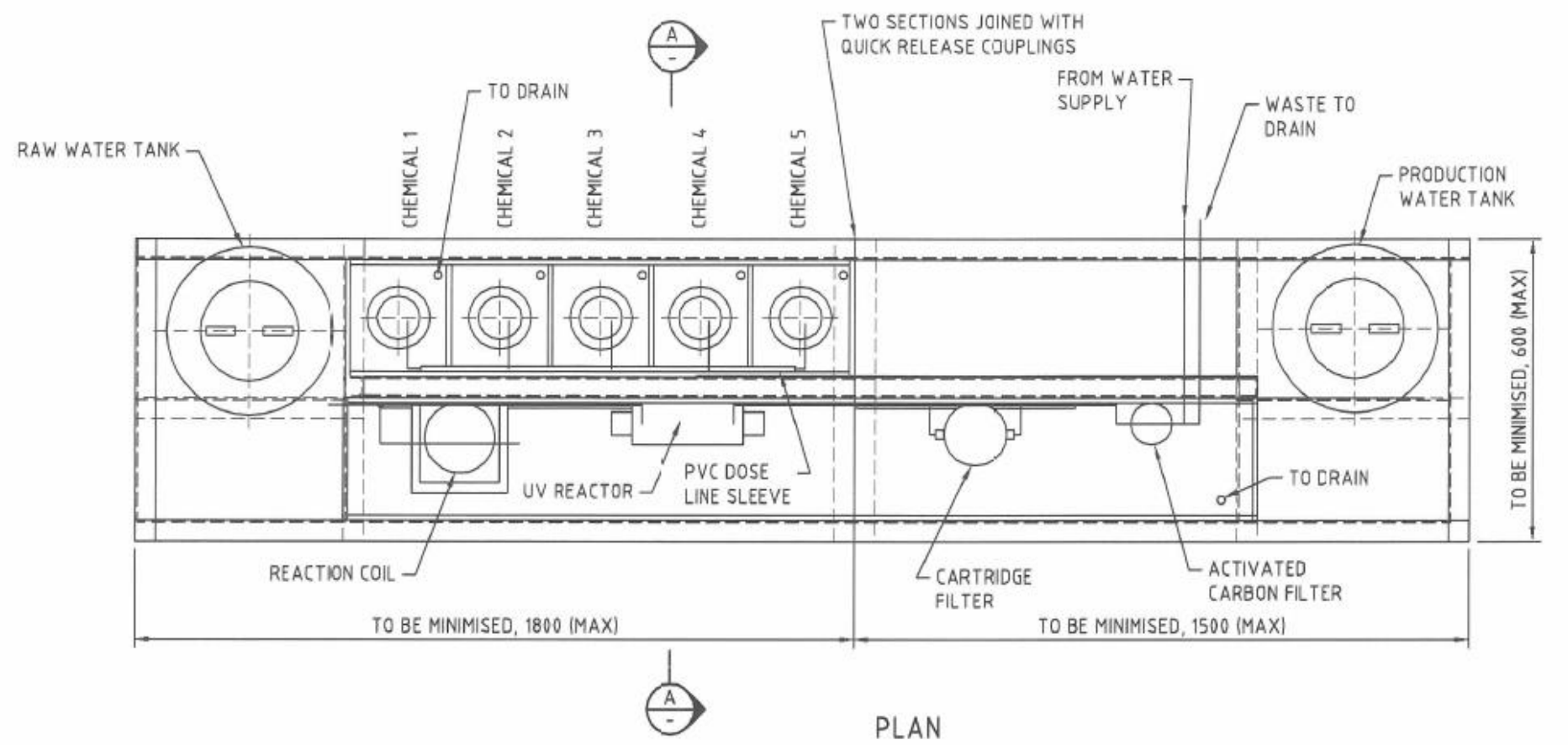
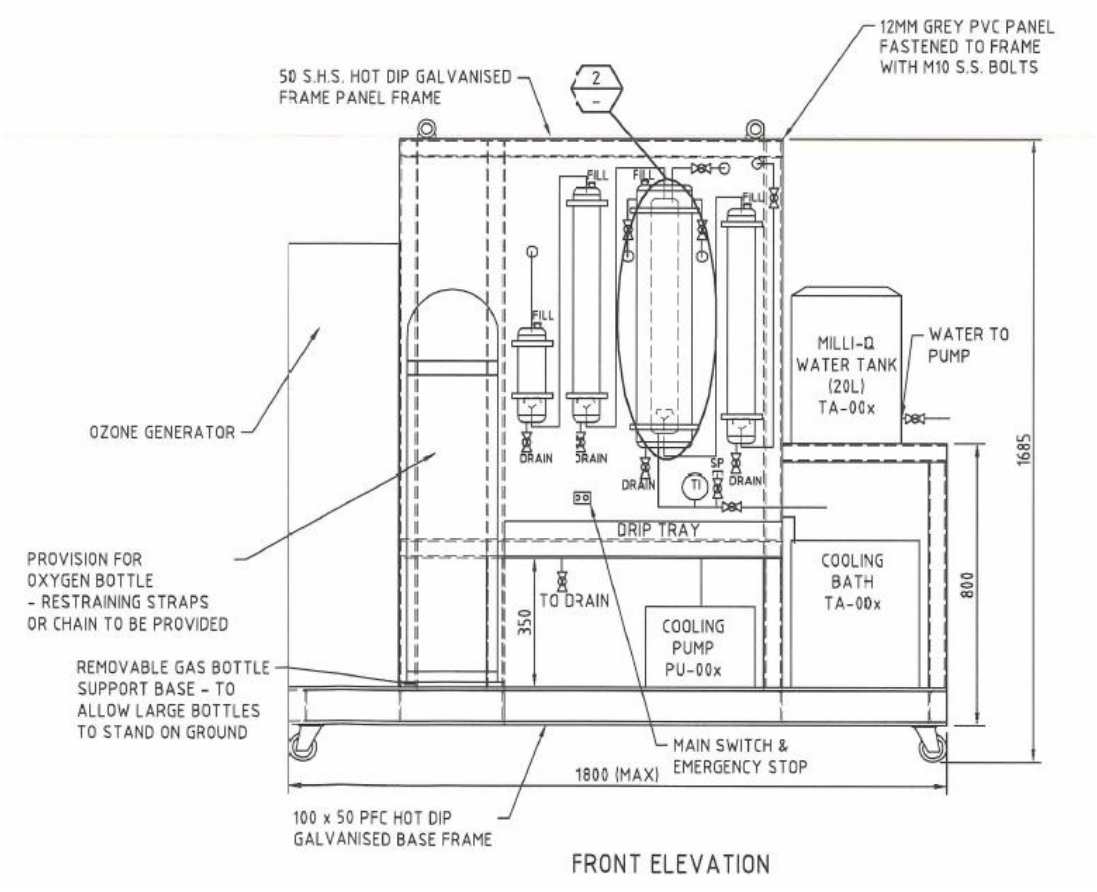
APPENDICES



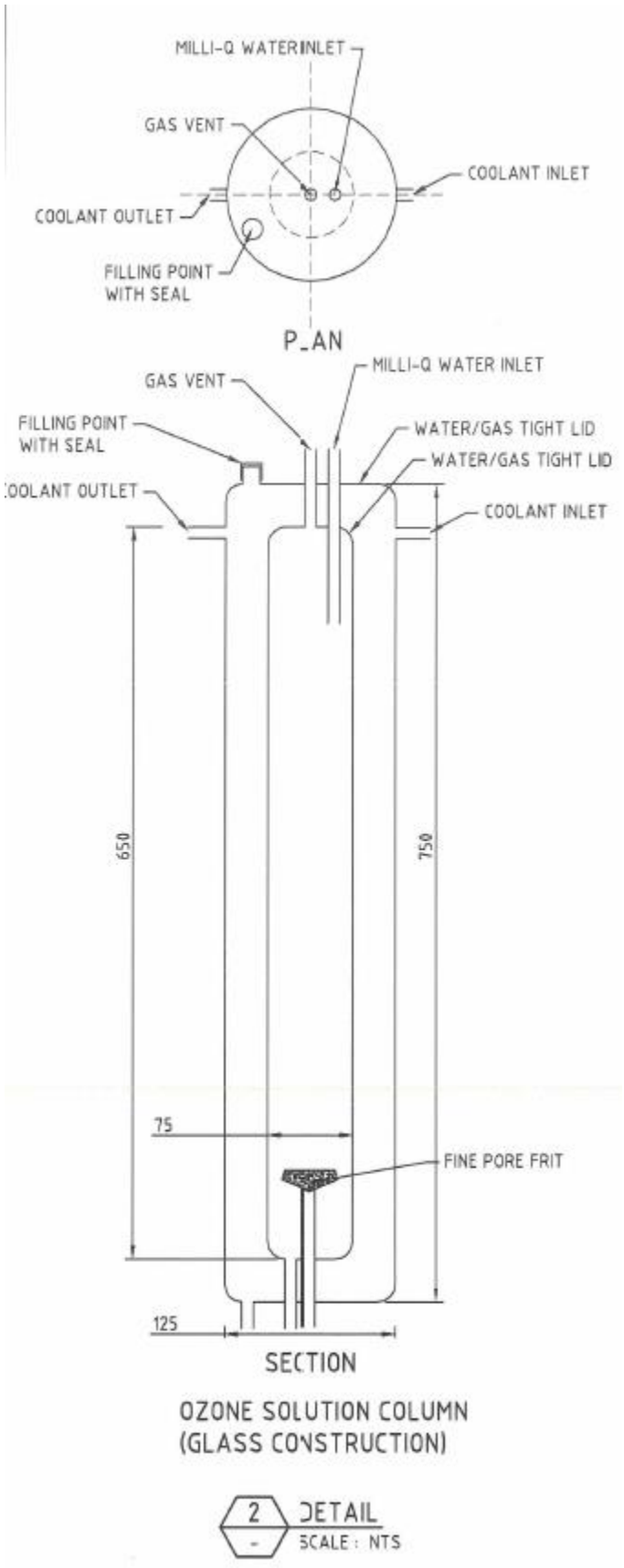
Appendix 2-1: Front view showing the detailed arrangement of the water treatment rig



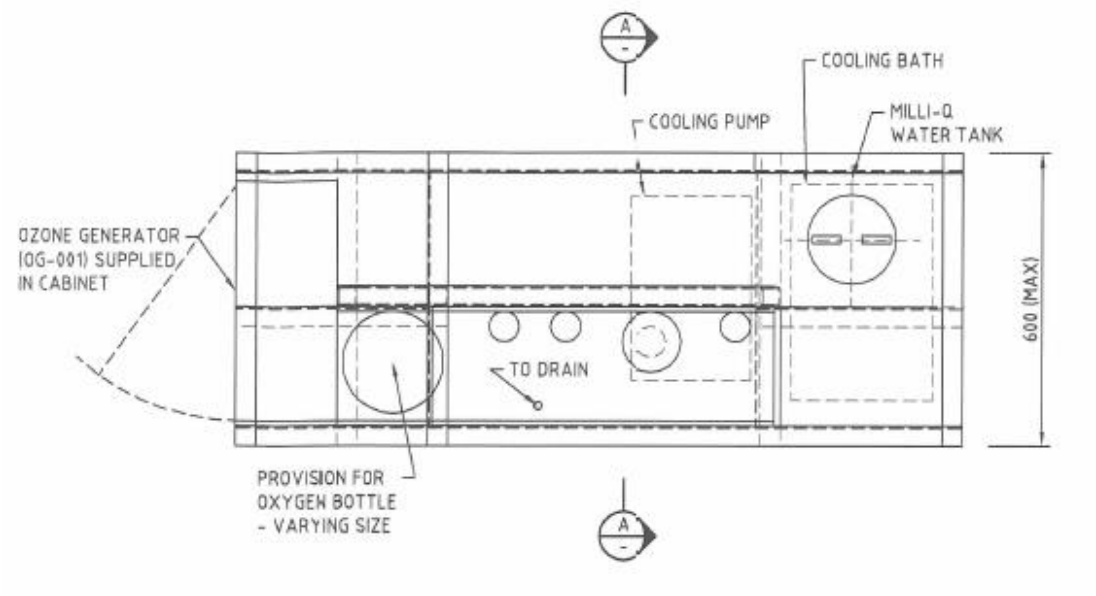
Appendix 2-2: Top view showing the detailed arrangement of the water treatment rig



Appendix 2-3: Front view showing the detailed arrangement of the ozonation module



Appendix 2-4: Close-up of the ozonation column



Appendix 2-5: Top view showing the detailed arrangement of the ozonation module