University of Southern Queensland

Faculty of Health, Engineering and Sciences

Monitoring and Removal of Natural Organic Matter (NOM) from Toowoomba Water Sources

A dissertation submitted by

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Abstract

Natural organic matter (NOM), present in all water sources, proves problematic for the water treatment industry due to its reaction with disinfectants, particularly chlorine. This reaction forms allegedly harmful, carcinogenic disinfection by-products. There are no regulatory limits in place in Australia for the quantifiable NOM surrogate parameter of organic carbon. Few studies have been conducted in Australia with the aim of quantifying the amount of NOM in water sources, with none having been conducted to investigate Toowoomba water sources.

The aim of this dissertation was to investigate the amount of organic matter in certain water sources of Toowoomba, the removal of this by enhanced coagulation, and the trihalomethane formation potential of each of the water sources before and after treatment. The methodology used to achieve this involved the collection of water samples from four water sources, three of which are drinking water sources for the Toowoomba region treated by the Mt Kynoch Water Treatment Plant. The water sources include the Japanese Gardens, Cooby Dam, Perseverance and Cressbrook Dams, and a raw water mixture of the blended raw water sources collected immediately prior to treatment from the Mt Kynoch Water Treatment Plant. Water samples were collected weekly for a ten-week period for the purpose of measuring the pH, turbidity, conductivity, total dissolved solids, alkalinity, dissolved organic carbon, ultraviolet absorption, iron and certain anions. Additional water samples were collected to conduct jar tests to investigate the removal of the organic carbon by enhanced coagulation. The jar tests were performed with alum as the coagulant being added in 10 mg/L increments up to 100 mg/L. Trihalomethane formation potential testing was also carried out.

In the absence of any Australian regulatory limits for organic carbon or treatment techniques, all experimental results for the Toowoomba water sources have been compared to the standards and practices in place in the United States.

Experimental results revealed the average dissolved organic carbon concentrations to be 4.51 mg/L, 7.29 mg/L, 5.75 mg/L and 5.26 mg/L for the Japanese Gardens, Cooby Dam, Perseverance Dam and the Mt Kynoch mixture respectively. Each of these values is greater than 2.0 mg/L, used in the United States as the trigger for the implementation of further treatment. If the organic carbon concentration of a raw water source exceeds this value, further treatment in the form of enhanced coagulation must be implemented. Therefore, it is recommended that further treatment is necessary for these Toowoomba water sources to target the removal of the excessive organic carbon present, in accordance with the regulations in place in the United States.

Jar test results demonstrated a decreasing trend in turbidity and dissolved organic carbon measurements with the increasing addition of alum. Optimum coagulant doses were selected based upon methods of analysis which involved identifying the point of diminishing return for each of the water sources. The optimum coagulant doses of alum selected were: 70 mg/L for both the Japanese Gardens and Perseverance and Cressbrook

Dams water sources; 90 mg/L for the Cooby Dam water source; and 60 mg/L for the Mt Kynoch raw water mixture. Treating the water sources with these alum doses resulted in organic carbon removal percentages of 36.2 percent, 33.1 percent, 32.0 percent, and 37.8 percent respectively. These jar tests were replicated to verify the results.

Equations were developed for each water source to theoretically predict the residual organic carbon from the coagulant dose. When treating the water samples with the selected optimum coagulant doses, the predicted residual organic carbon concentrations left untreated are 2.41 mg/L, 4.42 mg/L, 3.91 mg/L and 4.34 mg/L for the Japanese Gardens, Cooby Dam, Perseverance and Cressbrook Dams, Mt Kynoch raw water mixture water sources respectively.

The trihalomethane formation potential of the untreated water samples were measured to be: 132 ppb for the Japanese Gardens water; 209 ppb for the Cooby Dam water source; 250 ppb for Perseverance and Cressbrook Dams; and 231 ppb for the Mt Kynoch raw water mixture. Treating these water samples with the selected optimum coagulant dosages reduced the trihalomethane formation potentials to 22 ppb, 91 ppb, 146 ppb and 82 ppb respectively.

This research has contributed to quantifying the natural organic matter within Toowoomba's water sources, and investigating the removal of this by enhanced coagulation. Further research is recommended to better understand in more detail the topics covered by this dissertation.

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Certification of Dissertation

I certify that the ideas, designs and experimental work, results, analyses and conclusions set out in this dissertation are entirely my own effort, except where otherwise indicated and acknowledged.

I further certify that the work is original and has not been previously submitted for assessment in any other course or institution, except where specifically stated.

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Nomenclature

CRC   Cooperative Research Centre for Water Quality and Treatment

DBP   Disinfection By-Product

DBPR   Disinfection By-Product Rule

DOC   Dissolved Organic Carbon

NOM   Natural Organic Matter

NPOC   Non-Purgeable Organic Carbon

SUVA   Specific Ultraviolet Absorbance

TDS   Total Dissolved Solids

THM   Trihalomethane

THMFP   Trihalomethane Formation Potential

TOC   Total Organic Carbon

US EPA   United States Environmental Protection Agency

UV_{254} Ultraviolet at a wavelength of 254 nm

Chapter 1 Introduction

1.1. Background

Natural organic matter (NOM) is present in all surface waters as a complex variation of organic materials, produced by decaying vegetation, organic soils and biological activity. It is difficult to measure and so surrogate parameters are measured instead to give an indication of the concentrations present. These parameters include total organic carbon (TOC) and dissolved organic carbon (DOC).

NOM presents problems for drinking water purposes when it reacts with disinfectants such as chlorine, used in the treatment process and forms harmful disinfectant by-products (DBPs). There are many different compounds of DBPs but trihalomethanes (THMs) and haloacetic acids (HAAs) are examples of the most common ones of concern. The amount of NOM, or total or dissolved organic carbon, in a water source gives a direct indication of the amount of DBPs which can be formed. It is therefore an efficient and reasonable method to reduce the formation of these harmful compounds to target the removal of the organic matter. Effective removal of DBP pre-cursors is one of the major challenges in modern drinking water treatment (Ghernaout, Ghernaout & Kellil 2009).

In the United States, it is a regulated requirement that if any source water measures a concentration of greater than 2.0 mg/L of total organic carbon, a water treatment plant is required to practice enhanced coagulation. The Disinfection By-Product Rule, of the Environmental Protection Agency, stipulates monitoring and removal techniques and requirements for this process.

Other countries have regulations and guidelines for organic matter and DBPs in place to varying extents.

Nothing is regulated in Australia. In Australia, there are no guidelines or practices in place for the monitoring or removal or organic matter as DBP precursor material. There are guidelines, which are not regulated, in place for the concentrations of DBPs in drinking water.

In the absence of any Australian regulatory limits for organic carbon or treatment techniques, the data obtained from experimental testing for the Toowoomba water sources has been compared to the standards and practices in place in the United States for the purpose of this project.

1.2. Aim & Objectives

The overall aim of the project is to monitor the amount of natural organic matter (NOM) in certain water sources of Toowoomba and investigate the removal of this by enhanced coagulation.

To achieve this aim, the objectives which need to be satisfied include:

1. Collect water samples from Toowoomba water sources (Cooby Dam, Perseverance Dam, Japanese Gardens and the water immediately prior to treatment from Mt. Kynoch Water Treatment Plant) on a weekly basis.
2. Measure and analyse NOM-related characteristics of the water.
3. Perform enhanced coagulation to determine the dosage required for maximum NOM removal for each of the water sources by following the procedure described by the United States Environmental Protection Agency (US EPA) using alum as the coagulant.
4. Critically analyse the results obtained in Step 3 and evaluate the performance of the coagulant in removing the NOM.
5. Investigate the trihalomethane (THM) formation potential of raw and treated water using the optimum coagulant dosage.

1.3. Scope of Project

The scope of this research will identify the characteristics of the chosen water sources of Toowoomba to be monitored to give an indication of the amount of organic matter present in the water sources. An investigation into the removal of this matter by enhanced coagulation will also be conducted to determine the removal efficiency of using alum as a coagulant in each of the water sources. The testing of the effect of the use of different coagulants is not within the scope of the project. The investigation of the nature of the organic matter is also outside the project scope. The treated water at Mt Kynoch water treatment plant was not used for testing and so no conclusions can be made about the raw water after existing treatment processes occurring at the plant.

The limitations involved with this project include:

- There is a limited amount of time available for the completion of this project;
- All water sources supplying Mt Kynoch cannot be investigated separately; and
- NOM-related parameters will be measured only. Other measurements may provide additional information for this investigation but these are beyond the scope of what is being considered for the intention of this project.

1.4. Dissertation Outline

An outline is provided below for each of the remaining six chapters which make up this dissertation.

Chapter 2 – Literature Review

This chapter presents the background information for the investigated topic and discusses the studies previously conducted on this topic in Australia and overseas. The material covered in this chapter includes information regarding: natural organic matter; the problem of the formation of disinfection by-products; other problems associated with natural organic matter; the regulation of and policies concerning natural organic matter and disinfection by-products; the coagulation process; and the use of enhanced coagulation as a method of NOM removal. Previous studies have been investigated to identify their results and conclusions about waters in different areas. This investigation therefore pinpoints which waters have been studied and which have not, and the conclusions made about these waters (which may be directly or indirectly relevant to the topic of this project). The gaps in the literature, which this project intends to address, are identified from the research.

Chapter 3 – Methodology and Materials

Chapter 3 identifies and explains the materials and methodology used throughout the course of this project for the experimental work conducted. The sites at which the water sampling occurred are discussed in addition to the method that was followed to carry out the sampling. Descriptions of the testing processes when determining certain water characteristics can be found in this chapter. The details of the jar test used in the investigation of the NOM removal are also given.

Chapter 4 – Monitoring Process Results and Analysis

This chapter presents the results obtained from the initial monitoring period which tested the measured characteristics of the different waters. An analysis of the results presented here is completed to identify trends and explanations. The content of this chapter answers the question of whether further treatment (enhanced coagulation) is necessary for the waters of Toowoomba.

Chapter 5 – Jar Testing Results and Analysis

Chapter 5 discusses the investigation of the removal of the organic matter. The obtained results from the jar test procedure (outlined by the United States Environmental Protection Agency) are presented, with the analysis of these results. Methods of analysis are utilised to determine the optimum dosage required to achieve maximum organic matter removal. The removal of turbidity is also analysed and included in selecting an overall optimum coagulant dosage.

Chapter 6 – Trihalomethane Formation Potential Testing Results and Analysis

The results and analysis from the testing of the trihalomethane formation potential (THMFP) are presented in chapter six. Discussion of the raw water results and treated waters with the optimum coagulant dose of each of the water sources is included.

Chapter 7 – Conclusion and Recommendations

The final chapter reviews the obtained results to draw conclusions from the research and experimental work conducted for the project. The project's contribution to addressing the gaps in the literature is identified. Recommendations for further research, to supplement the work done for the purpose of this project, are also included in this chapter.

Chapter 2 Literature Review

This literature review covers an overview of natural organic matter and its associated problems such as the formation of disinfection by-products, the regulations and policies concerning organic matter and disinfection by-products, the coagulation and enhanced coagulation processes, and the previous studies that have been conducted. The gaps in the literature are identified from the research.

2.1. Natural Organic Matter

Natural organic matter (NOM) 'is defined as a complex matrix of organic materials present in all natural waters' (Anu Matilainen 2010). It consists of humic substances, amino acids, sugars, aromatic acids and a large number of other organic molecules (Agency 1999), some of which can be seen in Figure 2-1 . Humic substances account for approximately 50 percent of the dissolved organic carbon (DOC) in surface waters but this amount can fluctuate from each water source. 'These substances are formed by the biodegradation of plant and animal tissue in both soil and aquatic environments' (Agency 1999). 'NOM can be characterised in terms of its humic and non-humic fractions, its hydrophobic and hydrophilic nature and the molecular weights of its constituents' (Chow et al. 2009). NOM is universally present in all surface and ground water sources, in consequence of the interactions between the hydrological cycle and the biosphere and geosphere (Anu Matilainen 2010). Anthropogenic organic pollutants also contribute to organic matter from point and non-point sources along the waterways (Australia 2013). However in well-protected natural water, NOM is the largest source of organic matter compared to this synthetic organic matter and by-products from the treatment process which may also contribute to the organic matter content (Yan et al. 2006).
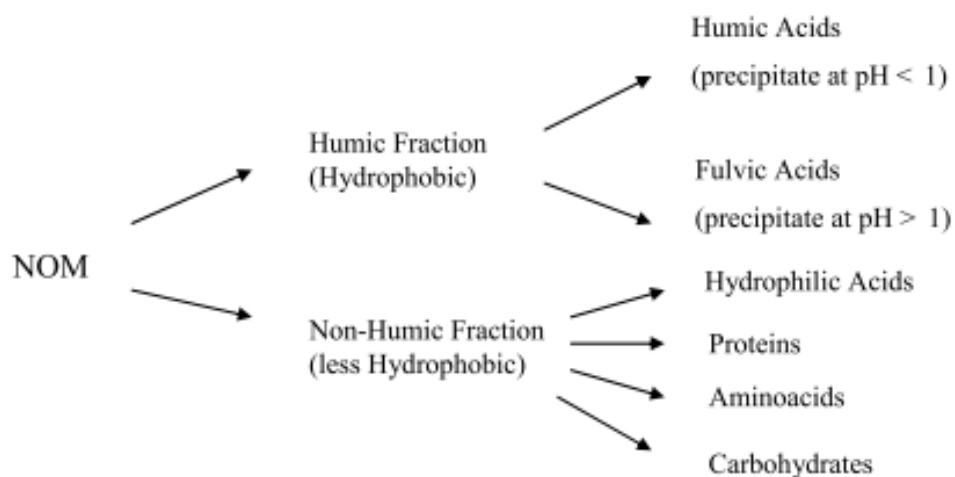
Figure 2-1   **Constituents of Natural Organic Matter (Garcia 2005)**

Over the past 10-20 years, an increase in the amount of NOM has been observed in raw water supplies in several areas worldwide, significantly affecting the drinking water treatment process. Anu Matilainen (2010) has suggested this is due to the changes in water availability and quality accompanied by climate change. This includes the effects of rainfall events, snowmelt runoff, floods and droughts.

2.2. Formation of Disinfection By-Products

Organic matter poses a problem when it reacts with disinfectants, especially chlorine, to form harmful disinfection by-products (DBPs).

Chlorine is widely used within the water treatment process for the purpose of disinfection. Disinfection is a crucial aspect of the water treatment process to remove disease causing pathogens. Chlorine is extensively used in water treatment plants globally, including throughout the United States and Australia. It is currently used as a disinfection agent at the Mt Kynoch Water Treatment Plant which treats the drinking water supply of Toowoomba. Pre-chlorination and post-chlorination both occur at two different stages in the water treatment process. Pre-chlorination is used to aid taste and odour control, turbidity control, algae growth control, inorganic oxidation, and microbial inactivation (Agency 1999). Post-chlorination involves the addition of chlorine to the water immediately prior to distribution to the population.

The occurrence of DBPs in chlorinated drinking water has been well documented (Andrzejewski et al. 2013). The concern is justified then that the organic matter present in the water will react with this chlorine at both points of pre- and post- chlorination to form harmful disinfection by-products. 'The amount of NOM present in the source water prior to chlorine addition bears a direct relationship on the amount and character of DBPs formed' (Australia 2013). 'More than 600 compounds of DBPs have been identified, among which trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common' (Anu Matilainen 2010). Trihalomethanes are disinfection by-products of particular concern. NOM consists of both particulate and dissolved components; however particulate organic matter does not significantly contribute to the formation of DBPs. Therefore, 'control of DOC becomes the critical factor in reducing the chemical risk of DBPs' (Australia 2013). Additionally, DOC accounts for approximately 90 percent of the total organic carbon in most waters (Garcia 2005).

The mechanism of DBP formation is not well understood. However, it is known that it involves substitution into the NOM producing organic halides and oxidation of carbon bonds (Garcia 2005).

2.3. Regulation of DBPs and THMs

Due to the possible adverse health effects, the 'concentrations of key DBP compounds in drinking water are regulated in many countries while in others such as Australia, guideline levels have been set by national health authorities, with some states moving to regulation' (van Leeuwen et al. 2011).

The Australian Drinking Water Guidelines provide guideline values for selected disinfection by-products. These are shown in Table 2-1.

Table 2-1   Guideline values for selected physical and chemical characteristics (Council & Council 2011)

Bromate	0.02 mg/L
Chlorite	0.80 mg/L
Dichloroacetic acid	0.10 mg/L
Trichloroacetic acid	0.10 mg/L
Total Trihalomethanes (TTHMs)	0.25 mg/L

In terms of THMs, 'separate guideline values were not derived for each compound' (Council & Council 2011). The monitoring and treatment of THMs is of particular importance in Australia to ensure these guidelines are adhered to because in major reticulated supplies, concentrations can range up to 0.6 mg/L (Council & Council 2011). However, guideline values in Australia are not absolute. 'Given the very conservative nature of the guidelines, deviations from the guideline values over a short period do not necessarily mean that the water is unsuitable for consumption. The amount by which and the period for which any guideline value could be exceeded without causing concern will depend on the chemical involved and other factors, such as the risks and benefits to public health' (Council & Council 2011).

THMs have been regulated in drinking water by the United States Environmental Protection Agency (US EPA), the World Health Organization (WHO), and the European Union (Andrzejewski et al. 2013). The US EPA regulate the THM concentration at 0.08 mg/L (Agency 1999). The countries of the European Union enforce a regulation of 0.1 mg/L for the THM concentration value in their water (Ghernaout, Ghernaout & Kellil 2009). Both of these values are much more stringent than the 0.25 mg/L Australian guideline value. The World Health Organization (WHO) does not give a guideline value for the total trihalomethane concentration, but instead states, 'the sum of the ratio of the concentration of each to its respective guideline value should not exceed 1' (Organization 2011). WHO gives the guideline values for these total trihalomethane constituents as those shown in Table 2-2.

Table 2-2   WHO Guideline Values for selected DBPs (Organization 2011)

Bromate	0.01 mg/L
Chlorite	0.70 mg/L
Bromoform	0.10 mg/L
Chloroform	0.30 mg/L
Bromodichloromethane	0.06 mg/L
Dibromochloromethane	0.10 mg/L

Additional examples of the regulation of THMs include the Iranian (Bahman Ramavandi 2015) and Korean (Kim 2005) regulations of 0.1 mg/L. The Turkish regulation had previously been 0.15 mg/L (Uyak et al. 2007) but the government changed this to 0.1 mg/L to comply with the EU regulations (K. Ozdemir 2013). Each of these values are more stringent that the Australian 0.25 mg/L guideline value. THMS are also regulated in Nicaragua at 0.46 mg/L (Garcia 2005).

More stringent regulations for DBPs are being suggested, particularly for DBPs other than THMs, due to health concerns regarding potential reproductive, carcinogenic and mutagenic effects (Australia 2013). Several researchers as cited by Garcia (2005) have found DBPs have a great influence on the occurrence of cancer, as well as growth retardation, urinary tract anomalies, spontaneous abortions and congenital cardiac defects. However, not all of the literature agrees on the same conclusion regarding the severity of the health effects. There is some dispute regarding the evidence to justify the health concern claims. Many studies have suggested there is an association between disinfection by-products and the occurrence of cancers, but the International Agency for Research on Cancer in 1991 (cited by Council and Council (2011)) concluded there is insufficient evidence to determine the carcinogenicity of disinfection by-products present in chlorinated drinking water.

2.4. Other Problems

Despite the removal of NOM from drinking water being primarily to reduce the formation of DBPs, there are other problems caused by NOM in drinking water and the water treatment process. It negatively impacts the water quality by creating colour, taste and odour problems; increased coagulant and disinfectant doses result in increased sludge volumes; biological growth is promoted in the distribution system; and there is an increased level of complex heavy metals and adsorbed organic pollutants (Anu Matilainen 2010). Disinfectant doses are increased because NOM creates a higher demand for it and water treatment plants are forced to increase the dose to maintain an adequate residual level in the water distribution system. Additionally, it has been shown NOM binds with harmful metals and synthetic organic chemicals which allows these contaminants to proceed through the water treatment process that do not facilitate the removal of NOM (Agency 1999).

2.5. Coagulation

Coagulation is the practice traditionally used in the water treatment process to remove turbidity from drinking water supplies. It is defined as 'a treatment process by which the physical or chemical properties of colloidal or suspended particles are altered such that agglomeration is enhanced to an extent that these solids will settle out of solution by gravity or will be removed by filtration' (Agency 1999). Coagulants are added to the water to change the surface charge properties of solids to promote this agglomeration of smaller particles into larger flocs which are removed by sedimentation and/or filtration. The selection of a coagulant depends on their ability to destabilise particles and to create a floc that can be readily removed by subsequent physical processes. 'The most widely used coagulant in drinking water production has been aluminium sulphate (alum)' (Anu Matilainen 2010). 'Aluminium and iron salts are typically used as primary coagulants because they are trivalent and form insoluble hydrolysed species that destabilise negatively-charged material in natural waters that keep particles in suspension' (Agency 1999). This process is not restricted to the removal of turbidity and so, with some modification to the process, can be utilised to remove some dissolved species as well including NOM.

2.6. Enhanced Coagulation

Enhanced coagulation is the process of obtaining improved removal of DBP precursors by conventional treatment (Agency 1999). This is achieved by increasing the dosage of the coagulant added typically in coagulation, optimized particularly for the removal of organic matter. Other changes may be made to the coagulation process including pH adjustment, changes in the order of chemical addition or the use of alternative coagulant chemicals (Anu Matilainen 2010). Maximised TOC removal is regarded as the unique objective of enhanced coagulation as opposed to optimised coagulation which aims to maximise turbidity, particulate TOC and DBP precursor removals, and minimise residual coagulant, sludge production and operating costs in practice in drinking water treatment (Yan et al. 2006).

The coagulation process removes NOM through four different means (Garcia 2005). NOM can combine with coagulants and precipitate. At high coagulant doses, it can be removed by either enmeshment or surface adsorption. It can also be removed through the chemical interaction of soluble NOM with soluble coagulant metal ions such as aluminium.

'The removal of natural organic matter (NOM) in conventional water treatment processes by the addition of coagulant has been demonstrated by laboratory research and by pilot-, demonstration-, and full-scale studies' (Agency 1999). Enhanced coagulation is described as the best available technology for the removal of NOM in the United States and is utilised in the country to target the removal of organic matter.

2.7. Policy in the United States

In the United States, the Environmental Protection Agency has implemented a rigorous strategy for the monitoring and removal of natural organic matter. This eventuated after the realization that providing maximum contaminant levels (MCLs) for selected disinfection by-products and maximum residual disinfectant levels (MRDLs) for selected disinfectants may not completely address the potential health risks from all disinfection by-products. A treatment technique requirement was then included in the existing Disinfection By-Product Rule (DBPR) to provide additional removal of natural organic matter, as measured by total organic carbon. Therefore, 'the purpose of the treatment technique for DBP precursor removal is to reduce the formation of DBPs. NOM reacts with disinfectants to form DBPs; therefore, lowering the concentration of NOM (as measured by TOC) can reduce DBP formation' (Agency 1999).

The publication 'Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual' (Agency 1999) explains in detail this Disinfection Byproduct Rule and treatment technique for the monitoring and removal of organic matter in place in the United States. The publication describes the details for both of the removal methods of enhanced coagulation and enhanced precipitative softening; however as only the investigation of enhanced coagulation is within the scope of this project, the details of the enhanced precipitative softening method will be omitted here.

The purpose of the Disinfection Byproduct Rule is to reduce the exposure to disinfection by-products by limiting allowable DBP concentrations in drinking water and by removing DBP precursor material to reduce the formation of DBPs (Agency 1999). This is achieved through the establishment of the maximum contaminant levels for selected DBPs, the maximum residual disinfection levels for selected disinfectants and the treatment technique for the removal of DBP precursor material.

Maximum Contaminant Level Goals (MCLGs) are developed as non-enforceable health goals, ' set "at the level at which no known or anticipated adverse effect on the health of the person would occur, and which allows an adequate margin of safety"' (Agency 1999). It is the policy of the EPA to set the MLCGs at zero for suspected human carcinogens. The Maximum Contaminant Levels (MCLs) are the legally enforceable standard and are set as close as possible to the MCLGs. The MCLGs and MCLs are shown in Tables 2-3 and 2-4.

Table 2-3   **MCLGs for the DBPR (Agency 1999)**

Bromoform	0.00 mg/L
Chloroform	0.00 mg/L
Bromodichloromethane	0.00 mg/L
Dibromochloromethane	0.06 mg/L
Dichloroacetic acid	0.00 mg/L
Trichloroacetic acid	0.30 mg/L
Bromate	0.00 mg/L
Chlorite	0.80 mg/L

Table 2-4   Legally enforceable MCLs for the DBPR (Agency 1999)

Total Trihalomethanes (TTHMs)	0.08 mg/L
Haloacetic Acids (HAA5)	0.06 mg/L
Bromate	0.01 mg/L
Chlorite	1.00 mg/L

TTHM is the sum of bromoform, chloroform, bromodichloromethane and dibromochloromethane.

As is a similar case, maximum residual disinfectant level goals (MRDLGs) are non-enforceable, health goals whereas the maximum residual disinfectant levels (MRDLs) are legally enforceable. These are shown in Tables 2-5 and 2-6.

Table 2-5   MRDLGs for the DBPR (Agency 1999)

Chlorine (as Cl_2)	4.0 mg/L
Chloramine (as Cl_2)	4.0 mg/L
Chlorine dioxide (as ClO_2)	0.8 mg/L

Table 2-6   Legally enforceable MRDLs for the DBPR (Agency 1999)

Chlorine (as Cl_2)	4.0 mg/L
Chloramine (as Cl_2)	4.0 mg/L
Chlorine dioxide (as ClO_2)	0.8 mg/L

The treatment technique, termed enhanced coagulation or enhanced precipitative softening, requires a specific percentage of influent TOC be removed during treatment to minimise the formation of DBPs. TOC is used as a surrogate for natural organic matter. All water treatment plants using surface water or groundwater under the direct influence of surface water that practice conventional treatment are obliged to comply with the treatment technique. 'A TOC concentration of greater than 2.0 mg/L in a system's raw water is the trigger for implementation of the treatment technique' (Agency 1999).

The treatment technique involves a two-step standard. The first step of the treatment technique includes TOC removal performance criteria which, if achieved, define compliance. The TOC removal percentages are shown in Table 2-7.

Table 2-7   Required Removal of TOC by Enhanced Coagulation (Agency 1999)

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO3)		
	0 to 60	**>60 to 120**	**>120**
>2.0 – 4.0	35.0%	25.0%	15.0%
>4.0 – 8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

The TOC removal percentages are dependent on alkalinity, as TOC removal is generally more difficult in higher alkalinity waters, and source water with low TOC levels (Agency 1999).

The second step of the treatment technique is in place for systems with more difficult-to-treat waters to demonstrate, through a specific protocol, an alternative TOC removal level for defining compliance (Agency 1999). This is achieved through conducting jar or bench scale testing.

2.8. Regulation of Organic Matter

The extent to which the United States has gone with the regulation of organic matter present in drinking water supplies is commendable and sets the standard for what should occur in other countries, as there are less stringent regulations for the removal of organic precursors than the disinfection by-products.

Some countries have followed in the footsteps of the US, and have taken measures to monitor the organic matter in the drinking water. For example, the national standards for drinking water in South Africa include a guideline value of 10mg/L of total organic carbon not to be exceeded (*South African National Standard Drinking water* 2011).

The Australian Drinking Water Guidelines omits any guidelines for the amount of organic carbon present in the water (Council & Council 2011). In the absence of Australian regulatory limits for organic carbon, this project has compared the measured data to the US EPA standards.

2.9. International Studies

Studies have been conducted worldwide into the formation of DBPs from organic precursors. Some examples are discussed here to highlight the areas in which the waters have been investigated, the objectives of the studies and the results obtained including the range of concentrations of organic carbon present in the waters. The character and amount of organic carbon varies geographically. As the concentration of organic matter differs geographically, so does the potential for the formation of THMs. 'In different geographical locations such as Spain, China, South Korea, Greece and US the average of THMs in the water treatment plants was stated in the wide range of 9-129 μg/L' (Bahman Ramavandi 2015). This highlights the significance of the site-specific nature of organic matter and the potential for the formation of DBPs.

The waters of Turkey have been extensively studied. Uyak and Toroz (2005) conducted a study which investigated the enhanced coagulation of Terkos Lake water of Istanbul City. Jar tests were completed with coagulants of aluminium and iron salts to determine the effectiveness for removal of the surrogate parameters TOC, ultraviolet absorbance, and THM formation potential. The results indicated that enhanced coagulation does increase the removal of DBPs precursors. Further study was completed by Uyak et al. (2007) on the same source water due to concerns surrounding the health effects of DBPs. It was concluded that supplementing enhanced coagulation with powdered activated carbon adsorption is more effective than enhanced coagulation alone.

A study conducted in Turkey by Avsar et al. (2014) investigated the Omerli and Buyukcekmece surface waters over a one year period to determine the disinfection by-product formation potential (DBPFP) of each of the fractions of the NOM content. It was concluded changes in the NOM content occurred on a seasonal basis and both surface waters contained THM and HAA precursors.

The Turkish waters were earlier investigated by Ciner and Ozer (2013) to determine the effects of different coagulants (including ferric chloride, aluminium sulphate and polyaluminium chloride) on the levels of organic matter removal of the Sivas Water Treatment Plant influent. The general characteristics of the raw water are shown in Table 2-8.

Table 2-8   **General characteristics of the Ciner and Ozer study (Ciner & Ozer 2013)**

Parameters	Range	Average
pH	8.02 - 8.25	8.15
Temperature (°C)	15.6 - 23.3	15.6
Conductivity (μs/cm)	318 - 393	363
Turbidity (NTU)	0.95 - 12.2	4.12
Colour (Pt-Co)	1.6 - 3.9	4.80
Alkalinity (mg/L as $CaCO_3$)	130 - 175	162.8
Chloride (mg/L)	7.4 - 8.7	8.20
Hardness (mg/L as $CaCO_3$)	160 - 180	172
UV_{254} (cm^{-1})	0.025 - 0.072	0.0393
DOC (mg/L)	2.51 - 4.19	3.547
SUVA (L/mg.m)	0.94 - 1.82	1.37

A study has recently been conducted in Iran. Bahman Ramavandi (2015) assessed 'the influence of the total organic carbon (TOC) content, chlorine quantity, water temperature, bromide ion concentrations, and seasonal variations on trihalomethanes (THMs) formation potential (THMFP) in Dez River water in Iran'. The maximum contaminant level (MCL) for THMs in drinking water according to Iranian regulation is 0.1 mg/L and it was found that the THMFP in the investigated water was relatively higher than this during summer times. The average values for the physical and chemical parameters of the Dez River water at the sampling point from this study are shown in Table 2-9.

Table 2-9   **General water characteristics from Dez River study (Bahman Ramavandi 2015)**

Parameters	Fall, 2012	Winter, 2013	Spring, 2013	Summer, 2013
pH	7.64	7.46	7.36	7.33
TOC (mg/L)	4.72	3.52	4.43	4.12
Water temperature (°C)	13.07	8.25	15.21	29.78
Hardness (mg/L CaCO$_3$)	160	122	131	150
Alkalinity (mg/L CaCO$_3$)	137	104	109	134
Br$^-$ (µg/L)	161	127	132	157
Turbidity (NTU)	7.86	8.96	8.08	8.53

Garcia (2005) investigated the existence of trihalomethanes in a drinking water plant in Nicaragua to determine if the concentrations exceeded the US EPA maximum contaminant level and Nicaraguan guidelines. A comparison was made between the ability of the conventional and enhanced coagulation processes to remove natural organic matter. The study concluded the average THM concentrations were below both the US EPA and Nicaraguan guidelines. The comparison between the water treated by conventional and enhanced coagulation revealed enhanced coagulation considerably diminished the THM formation and the value never exceeded the guidelines.

Raw water from a drinking water plant in Nicaragua was investigated in a later study by Garcia and Moreno (2007). Similar in scope to this project, enhanced coagulation was investigated to determine how it reduces the presence of NOM and decreases the THMs formation. It was concluded that enhanced coagulation does strongly reduce the presence of organic matter, which significantly decreases the formation of THMs. This is due to the use of higher alum doses in comparison with conventional coagulation utilized at the facility. The removal of DOC is typically 44% at the facility, and was improved significantly to 67% through the use of enhanced coagulation. The formation of THMs was further studied by varying pH, contact time, temperature and chlorine dose. The obtained results indicated THM concentrations exceeded the US EPA maximum contaminant level of 0.08 mg/L in extreme conditions but not the Nicaraguan target value of 0.46 mg/L for both conventional and enhanced coagulation.

A study conducted in India on the water from the Kansawati River by Narayan and Goel (2011) was a similar investigation to this project. The characteristic parameters of the water were measured (UV absorbance, microbial concentrations, TDS, conductivity, hardness, alkalinity and pH). The optimum coagulant doses for turbidity and TOC removal, and the TOC removal percentage, were then determined by conducting jar tests with alum used as the coagulant. The water was characterised as low TOC (<2mg/L), high alkalinity water. Two samples were collected and tested four months apart. The results concluded the optimum alum dose for the removal of turbidity and TOC was 20mg/L for the first sample, and 100mg/L for the second sample. The TOC removal percentage increase was insignificant compared to the increase in coagulant dose required.

The efficiency of polyacrylamides for NOM removal was investigated in Brazil by Conticelli et al. (2008).

Dhaouadi et al. (2013) studied the optimum coagulation conditions to minimise dissolved organic matter in the water of the Koudiat Medouar dam in east Algeria.

Numerous studies have been conducted in South Africa. The waters of South Africa were studied by Dlamini et al. (2013) when eight different raw water samples from the various water types of the country were seasonally collected and treated by enhanced coagulation using ferric chloride as the coagulant (due to its extensive use as a coagulant in the water treatment industry in South Africa). The South African surface water sources have additionally been investigated by Lobanga, Haarhoff and van Staden (2014) in their study that established a correlation to estimate the coagulant dosage for any desired level of UV_{254} absorbance removal, again using ferric chloride as the coagulant.

Nkambule et al. (2012) earlier studied the nature, composition and character of NOM in South African waters. This was achieved by sampling eight different water treatment plants, the application of conventional techniques and then further NOM characterisation was conducted using advanced techniques. The DOC measurements were within the range of 3.5 to 22.6 mg/L.

Enhanced coagulation is not a mandatory requirement in Korea, similar to Australia. The applicability of the US EPA's criteria for removal of TOC with enhanced coagulation was studied for Korean waters by Kim (2005). The results indicated the US EPA criteria were achievable for the Korean waters. Similarly, this project aims to determine the applicability of the criteria to the waters of Toowoomba. The waters of Korea were further studied by 정영미, Kweon and Lee (2007) when water from Han River was used to investigate the effects of different raw water qualities on enhanced coagulation. This study was also guided by the US EPA requirements.

The measurement and removal of NOM has been the topic of many studies in China. A study was conducted at a water treatment plant in China by Liu et al. (2012) to determine feasible technological strategies to enhance the removal of NOM and minimise the formation of DBPs for sources water with high concentrations of NOM.

An extensive study by Wang et al. (2013) further investigated 29 source waters in China. The chemical and physical characteristics of the dissolved organic matter (DOM) were examined in relation to geographical location and seasonal variation. The treatability of the waters by enhanced coagulation with four different coagulants was also investigated. The source waters were able to be characterised by their qualities. For example, waters of east China were generally of low DOM content, low SUVA and high molecular weight DOM.

Enhanced coagulation was also earlier investigated by Yan et al. (2006) at a North China water treatment plant. The characteristics of the typical source water of northern China and their enhanced coagulation features were determined. The results revealed it to be a high alkalinity and pH water with a composite coagulant (HPAC) being more effective at removing organic matter than the traditional coagulants used.

Raw water from Singapore has been studied by Qin et al. (2006) when the effect of coagulation pH on enhanced removal of NOM in treatment of reservoir water for drinking purposes was investigated. Jar tests were conducted with different coagulation pHs and alum dosages. NOM removal, in terms of DOC, of up to 45% was achieved during tests at optimal conditions, whereas only a 35 percent DOC removal was achieved with conventional coagulation. This concludes that the optimisation of conditions for NOM removal is critical.

There has been a case study in Serbia (Tubic et al. 2010) where the removal of NOM, in addition to arsenic, with the use of a combination of different coagulants was investigated.

Szlachta and Adamski (2009) were responsible for a case study in Poland which investigated the efficiency of NOM removal from the water of the Odra River. The processes of alum coagulation and PAC-adsorption were tested, with the results indicating the PAC-adsorption to be the more efficient process for NOM removal.

A study was conducted by Sulaymon, Ali and Al-Naseri (2009) to determine the amount of NOM and its disinfection by-products formation potential for the Tigris River water in Baghdad. The results concluded the raw water TOC levels have the potential to produce concentrations of THMs which would exceed the US EPA guidelines for most of the duration of the year. Enhanced coagulation presently is

capable of reducing NOM to an acceptable level according to these US EPA requirements.

Sharp et al. (2005) compared case study sites in the US and the UK across periods of elevated organic levels to give evidence of the temporal and spatial variation in NOM composition and characteristics. For example, during the period of April to June 2004 in raw Poudre River water (in the US) DOC levels increased rapidly from 3.5 to 7.4 mg/L as a direct result of the spring snowmelt runoff.

While analyses of DOC in confined regions have been numerous as exemplified by the case studies that have been discussed, there have been very few attempts at achieving this analysis on a global scale.

An extensive investigation into the increase of natural organic matter was documented by Marc Philibert et al. (2011). Long term data including TOC measurements were retrieved from 23 sites worldwide, mainly from France, United Kingdom, Germany and North America. Of the 23 sites, 13 sites in North America, UK and France showed an increase in NOM, measured as TOC. This worldwide trend of increasing NOM was often accompanied by an increase in water temperatures, a likely consequence of climate change. An increase in NOM has also been documented in other studies in the United States, Canada, Norway, the Czech Republic, Sweden and the UK as cited by Marc Philibert et al. (2011).

In 2003, Xenpoulos et al. (cited by Sebastian Sobek and Lars J. Tranvik (2007)) examined data from 745 lakes in 11 geographical locations.

Sebastian Sobek and Lars J. Tranvik (2007) later assembled a much larger database of DOC concentrations and other parameters that characterise the conditions in the lakes, the catchment, the soil and the climate for 7,514 lakes from six continents, in an attempt to better understand the factors that regulate DOC in lakes. Data was collected from the published literature, unpublished studies and national lake surveys to obtain the DOC concentrations, which are shown graphically in Figure 2-2 by the different coloured points on the map. As can be observed, large areas of the world are still underrepresented or completely missing from the dataset. In particular, attention should be brought to the fact that, even in a study as comprehensive as this, Australia is completely missing from this dataset. There was no data available for collection for the inclusion in this study for any Australian waters. Despite this, the dataset covers a wide climatic gradient that stretches from the high Arctic to the subtropics which allowed the analysis of the relationship between lake DOC concentration and climatic conditions.

The DOC concentrations were within the range of 0.1 to 332 mg/L (Sebastian Sobek and Lars J. Tranvik 2007). DOC concentrations of between 1 and 20 mg/L were most common – found in 87 percent of the lakes. Concentrations of less than 1 mg/L were recorded in 8.3 percent of the lakes, while 4.2 percent of the lakes had a DOC concentration of between 20 and 40 mg/L. Only 0.4 percent of the lakes recorded DOC concentrations of greater than 40 mg/L. The results were compared to the other

parameters that characterise the conditions in the lake. It was concluded there is a hierarchical regulation of DOC in lakes, where climate and topography regulate the terrestrial vegetation, soils and hydrology within one region which sets the range of possible DOC concentrations in the lakes. Then, in each individual lake of that region the DOC concentration is regulated by the local lake and catchment parameters such as the proportion of wetlands and upstream lakes, and the water retention time. An additional conclusion from the study was the demonstration of the sensitivity of lake ecosystems to climate change due to the strong correlation demonstrated among climate, catchments and the biogeochemistry of lakes. Changes in climate will affect the DOC concentrations in lakes which will have significant effects to the ecosystem structure and function. Sebastian Sobek and Lars J. Tranvik (2007) admit 'there are important gaps in the global coverage of our data set, especially at low latitudes. To improve our understanding of the climate and catchment regulation of lake ecosystems, future work should strive to fill these gaps'. This project aims to contribute to filling that identified gap.
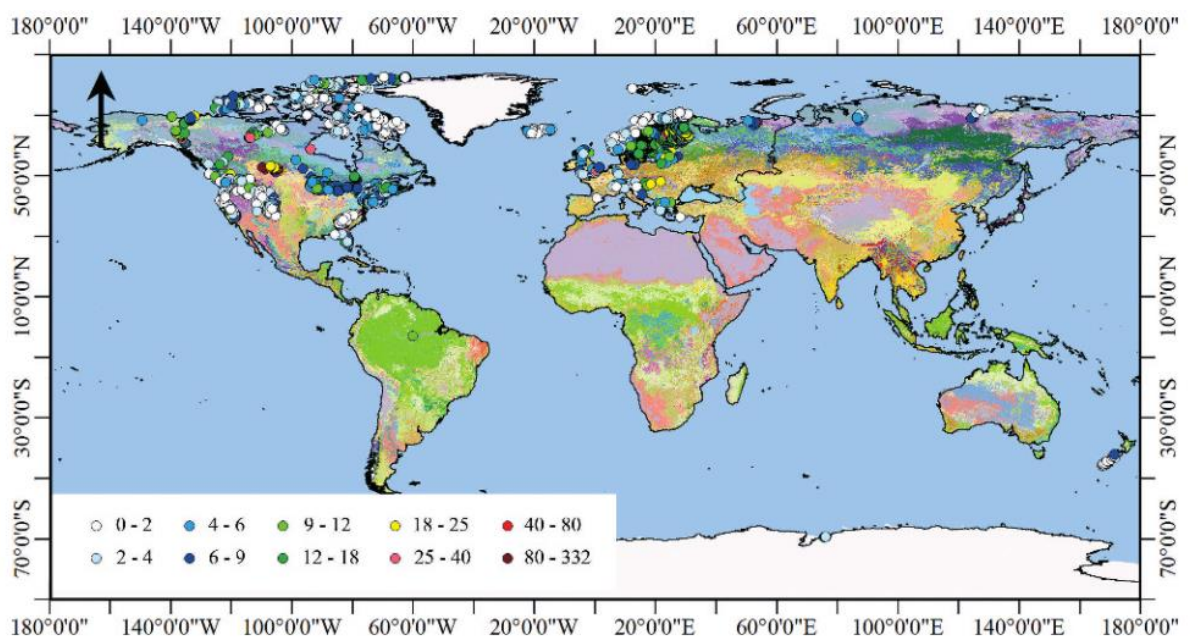
Figure 2-2 **DOC concentrations, as indicated by the coloured points, from the global study (Sebastian Sobek and Lars J. Tranvik 2007)**

These case studies have been discussed to give an indication of the studies which have been conducted in this field of research, their specific aims and objectives, some of the results and conclusions made and the locations in which they were conducted. As can be observed, the study and investigation of natural organic matter within water sources has been conducted haphazardly in different geographic locations worldwide. In some areas it has been investigated extensively and thoroughly while in others, there is a lack of knowledge due to the absence of any literature. A more in-depth look at the studies conducted in Australia is necessary to determine the extent of what has been done in this country and in which locations.

2.10. Australian Studies

The waters within Australia have sporadically been investigated through studies. Some of which are described as follows to give an indication of the water in which areas have been studied and the results which have been obtained for those areas.

The raw water from the Murray River used in the Morgan Water Treatment Plant in South Australia was investigated in a study conducted by Aslam et al. (2011) to determine the removal of DOC in relation to its character by application of various coagulant doses and also to determine the applicability of using a peak fitting technique to analyse high performance size exclusion chromatography (HPSEC) data for determination of treatability of NOM in water. The conclusions from this study included: the removal of higher molecular weight compounds (humic substances) occurred more easily than the removal of lower molecular weight compounds (non-humic substances), and a model was developed to enable the prediction of percentage area removal by coagulation, designed using peak fitting data for HPSEC molecular weight profile of treated water (Aslam et al. 2011).

An additional study was carried out in South Australia by Braun et al. (2014) to provide a comparative assessment of four parallel surface water treatments during the 2010-2012 inflows to the Murray-Darling Basin as a result of the flooding which occurred during that period. The four water treatment processes assessed included: conventional coagulation, magnetic ion exchange (MIEX)/coagulation, with and without granular activated carbon (GAC), and membrane treatment combining microfiltration (MF) and nanofiltration (NF), which were challenged by the high levels of organic matter and turbidity in the waters at the time. The study concluded that 'all four processes could effectively meet basic water quality guidelines of turbidity and colour despite challenging source water quality but that the more advanced treatments improved overall organic and bacterial removal' (Braun et al. 2014).

A study, with objectives more closely aligned to those of this project, was carried out by Chow et al. (2009) to investigate the characterisation of the NOM content in raw water samples from four Australian reservoirs and then to assess the removal of this NOM by alum coagulation. The reservoirs – Hope Valley, Myponga, Moorabool and Mt Zero – are located in either South Australia or Victoria. The results showed that after optimised alum coagulation all four waters had a similar character, despite the organic character of the four source waters originally differing. 'The molecular weight distribution analysis (HPSEC) indicated alum coagulation preferentially removed the higher molecular weight UV absorbing compounds whilst those remaining in the treated waters had the properties of lower apparent molecular weights and less UV absorbance' (Chow et al. 2009). The summary of source water quality parameters for the four Australian reservoirs is shown in Table 2-10.

Table 2-10   Water characteristics measured in the study of Australian reservoirs (Chow et al. 2009)

Parameter	Hope Valley	Myponga	Moorabool	Mt Zero
pH	8.0	7.6	7.6	6.4
Turbidity (NTU)	2.9	1.7	1.7	7.3
Colour (HU)	16	64	17	54
Alkalinity (mg L^{-1} as CaCO$_3$)	80	57	100	7.0
Mw (Daltons)	1200	1600	1000	1000
UV$_{254}$ (cm^{-1})	0.147	0.434	0.178	0.265
DOC (mg L^{-1})	5.0	10.8	6.9	9.0
SUVA (m^{-1} mg^{-1}L)	3.0	4.0	2.7	2.9

van Leeuwen et al. (2011) has studied the waters in Victoria and South Australia for the purpose of developing mathematical models to describe the relationship between the formation of THMs and bromide concentrations, pH and temperature. These waters were tested under standard conditions and so the results cannot be used to draw any site-specific conclusions about the characteristics of the water.

Water treatment plants have been investigated in Adelaide earlier by J. van Leeuwen (2009) for the purpose of implementing the mEnCo software for coagulant dose determination.

Additional earlier work by J. van Leeuwen (2005) used models which were applied to waters from Googong (Australian Capital Territory) and Middle (South Australia) River Reservoirs to predict required alum doses. Within the study, similar analysis to that outlined by the US EPA was completed. THMFP testing was also conducted, with the formation of individual THMs found to be highly consistent for each water but varied significantly between the two waters.

A study conducted by Varcoe et al. (2010) had a specific scope, which investigated the impact of gypsum application to pasture on the concentration and character of DOC in the Mount Lofty Ranges of South Australia. The results concluded gypsum application to certain soils has potential to enhance their capacity to bind NOM, and thereby lowering DOC concentrations.

A study by Kristiana, Joll and Heitz (2011) investigated the impact of the addition of powdered activated carbon to an enhanced coagulation treatment process at an existing water treatment plant in Western Australia on the NOM removal effectiveness. It was the 'first comprehensive assessment of the efficacy of plant-scale application of PAC combined with enhanced coagulation on an Australian source water' (Kristiana, Joll & Heitz 2011). The NOM removal improved by 70 percent as a result of the powdered activated carbon and also reduced the formation of DBPs by 80-95 percent.

The testing of a polyaluminium chloride and chitosan composite coagulant was conducted in a study by Mega Ng et al. (2011) in Australia with water from Myponga

Reservoir in South Australia (earlier investigated in another study). The effectiveness of the coagulant for the removal of organic matter was examined from this natural water and a synthetic water.

Research projects of the Cooperative Research Centre for Water Quality and Treatment have been conducted to understand the character of NOM in Australian water supplies and assess its impact on water quality. A range of treatment options were evaluated for the removal of NOM.

DOC concentrations of Australian waters were measured and the results were quite diverse (CRC n.d.). They ranged from very low in the eastern states of New South Wales and Victoria, and the Northern Territory to very high in South Australia and Western Australia. The difference after treatment is shown graphically in Figure 2-3. The treatment was optimised for the South Australia and Western Australia water supplies with high DOC 'to obtain significant removal whereas the New South Wales treatment plants with lower DOC values are not optimised to remove DOC to the same extent' (CRC n.d.). It can be observed the only data for Queensland is the one Hinze location. The survey of nine water samples from around Australia over a 24 month period revealed all water sources experienced seasonal variation in DOC concentration.

Rapid Fractionation (RF) divides NOM into four organic fractions of: very hydrophobic acids (VHA); slightly hydrophobic acids (SHA); hydrophilic charged (CHA); and hydrophilic neutral (NEU). As shown by Figure 2-4, the RF of Australian water supplies indicate that waters with higher DOC concentrations tend to have a higher proportion of hydrophobic fractions (VHA & SHA) whereas lower DOC concentrations correlate with higher proportions of the hydrophilic neutral (NEU) fraction. 'Most waters surveyed in Australia tended to have very low concentration of CHA and NEU fractions with the greatest concentration of the DOC present as hydrophobic fractions (VHA/SHA)' (CRC n.d.).

Enhanced coagulation with an increased alum dose increases the removal of the VHA and SHA fractions and, to a lesser extent, the CHA fraction but not the NEU fraction. This results in the character of the treated water differing greatly from the character of the raw water. Results indicated coagulation preferentially removes higher molecular-weight, UV absorbing compounds and leaves lower molecular-weight, less UV absorbing compounds in the treated water. The CHA, VHA and SHA fractions are most easily removable by coagulation whereas most of the NEU fraction will be recalcitrant to removal by conventional treatment. Therefore, the higher the proportion of the fractions amenable to removal that are present in the water, the greater the amount of DOC that will be able to be removed by coagulation (CRC n.d.).

DOC levels in Australia - Snap shot from early 2003
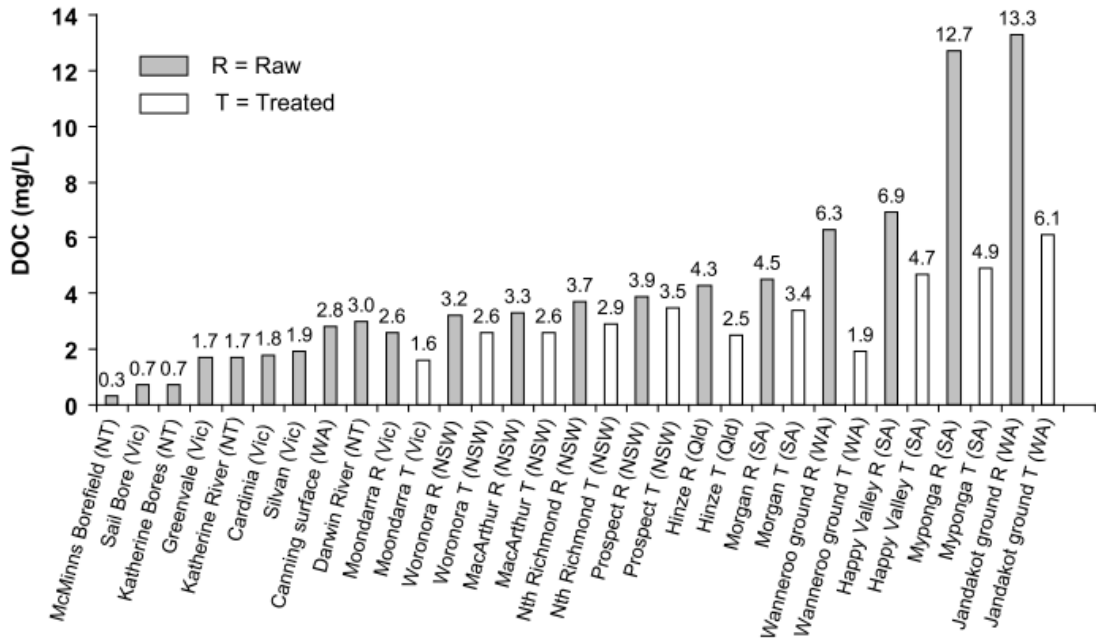
Figure 2-3 **DOC concentrations before and after treatment for particular water sources (CRC n.d.)**

Snap Shot in 2003

DOC: 1 - 3 mg/L
VHA: 19 - 38 %
SHA: 14 - 25 %
CHA: 6 - 7 %
NEU: 33 - 50%

DOC: 1 - 6 mg/L
VHA: 35 - 58 %
SHA: 12 - 24 %
CHA: 6 - 8 %
NEU: 19 - 26 %

DOC: 6 - 13 mg/L
VHA: 60 - 82 %
SHA: 7 - 21 %
CHA: 4 - 6 %
NEU: 7 - 22 %

DOC: 2 - 3 mg/L
VHA: 40 - 54 %
SHA: 15 - 23 %
CHA: 5 - 9 %
NEU: 20 - 32 %

DOC: 5 - 14 mg/L
VHA: 50 - 70 %
SHA: 15 - 25 %
CHA: 5 - 17 %
NEU: 6 - 16 %

DOC: 1 - 2 mg/L
VHA: 16 - 40 %
SHA: 15 - 31 %
CHA: 5 - 8 %
NEU: 20 - 56 %

NT

QLD

WA

SA

NSW

Vic
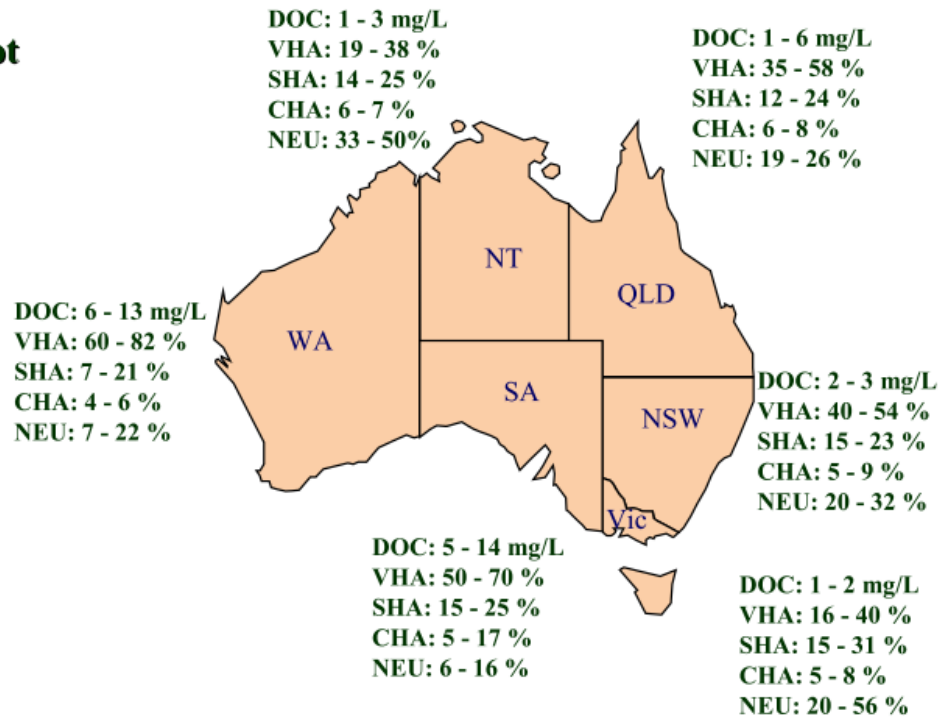
Figure 2-4   **Average DOC concentrations for each state and the organic fraction proportions (CRC n.d.)**

These studies have been discussed to bring attention to the work which has been conducted in Australia in this field of research and where further work is required. The measurement of organic matter and the potential for DBP formation in water sources has not been investigated equally throughout Australia. The water sources of some areas, such as South Australia, have had been thoroughly investigated, whereas there is a complete lack of research conducted in others such as Queensland. The importance of conducting this research on a site-by-site basis should be emphasised due to the geographical variance in NOM concentrations. Therefore, it can be suggested that research must be conducted in specific areas to be able to gain any knowledge on this topic for a particular location and its water sources. This is true for Toowoomba, Queensland.

2.11. Literature Gap

Through the study of waters in Australia and overseas, the waters can be attributed with certain characteristics. For example, it has been identified that streams and water storages in southern Australian have relatively high levels of natural organic matter that appear to be related to the nature of its soils and climate (Varcoe et al. 2010). However, there has been no record identified of an investigation into the waters of Toowoomba, and hence there is a complete lack of knowledge for this area in terms of NOM concentrations in the water sources and the potential for the formation of DBPs.

The investigation of Toowoomba waters has not been included in any studies examined for the purpose of this literature review, and consequently the contribution of this project intends to fill this gap in the available knowledge.

2.12. Chapter Summary

This chapter reviewed the literature relevant to natural organic matter and its associated problems, with particular attention on the formation of disinfection by-products. Descriptions of the involvement of the coagulation and enhanced coagulation processes in water treatment were provided. The different policies and regulations in place and previous studies relevant to the investigated topic were discussed. Literature gaps were identified.

Chapter 3 Methodology and Materials

This chapter describes the methodology and materials used for the experimental work carried out for this dissertation. The sites at which the water samples were collected from are discussed in addition to the method that was followed to undertake the sampling. Descriptions are given of each of the testing processes as to determine the analytical measurements. The experimental procedures for both the jar testing and trihalomethane formation potential testing are also outlined.

3.1. Sampling Sites

Water samples will be collected from four different Toowoomba water sources. Three of which will be collected from different points at the Mt Kynoch Water Treatment Plant and the fourth sample will be collected from the Japanese Gardens.

The Mt Kynoch Water Treatment Plant supplies water to Toowoomba and the surrounding areas (such as Highfields, Crows Nest, Oakey and Goombungee) for domestic and industrial use. Each day, up to 68 million litres of water is treated to a standard suitable for human consumption through the use of the conventional water treatment processes of coagulation, flocculation, sedimentation, filtration and disinfection (Council 2011).

Town bores account for up to thirty percent of Toowoomba's water supply. The remainder of the water used by the Mt Kynoch Water Treatment Plant is sourced from Cressbrook, Perseverance and Cooby Dams.

The construction of Cooby Dam was completed in 1941, making it the oldest dam to supply water to Toowoomba. It is located 17km north of Toowoomba in the Condamine Balonne catchment. The catchment area spans approximately 160 km^2. The total maximum available storage is 21,166 ML, but the full water supply useable capacity is 19,703 ML. With a full supply, the storage area is 306 hectares. There are three pumps inside the pump station and the raw water is lifted almost 120m to the Mt Kynoch Water Treatment Plant (Council 2015a).

Cooby Dam is used for many recreational activities but swimming is excluded. Fishing and boating (with electric motors) are allowed on the water, with walking trails and picnic areas having been provided in the surrounding area (Council 2015b).

Perseverance Dam is located approximately 35km northeast of Toowoomba with a total catchment area of 110 km^2. The construction of which was completed in 1965. Accounting for a full supply, the total storage area is 250 hectares. The dam has a supply useable capacity of 26,893 ML but a maximum storage capacity of 30,140 ML (Council 2015a).

Unlike Cooby and Cressbrook Dams, fishing and boating are not permitted at Perseverance (Council 2015b). Picnic and barbeque areas are provided for the main recreational use of the area.

Cressbrook Dam is the largest and the most recently constructed of the three dams. Construction was completed in 1983, with a storage area for full supply of 517 hectares. The maximum capacity is 81,842 ML but with only a storage of 78,847 ML as a useable supply. Cressbrook Dam is located approximately 10km downstream of Perseverance Dam on Cressbrook Creek with a total catchment area of 320km^2 including Perseverance (Council 2015a).

Cressbrook has similar recreational uses to Cooby Dam, in addition to camping being allowed. Water activities are permitted on the dam such as boating, canoeing, windsurfing and sailing (Council 2015b). As is the case with the other dams, swimming is prohibited.

The Japanese Gardens is a park located on the northern side of the University of Southern Queensland Toowoomba campus, designed for peaceful leisure. "It is one of Australia's largest and most traditionally designed Japanese stroll garden" (Queensland 2015).

The garden includes a central lake, stream, waterfall, pathways, lawns, and Japanese and Australian native trees and plants. The area is popular with wildlife with many species of fish and birds residing in the garden.

The water samples to be collected from the Mt Kynoch Water Treatment Plant will include a water sample of the raw water sourced from Cooby Dam, a water sample of the raw water sourced from Perseverance Dam, and a water sample of the blended raw water sources immediately prior to treatment for consumption. Typically, the water sample containing the raw water from Perseverance Dam would also contain raw water from Cressbrook Dam but there will be no water pumped from Cressbrook Dam (and consequently used by Mt Kynoch) during the period that the water samples will be collected. On some of the days which samples are to be collected, a small percentage of supernatant water may also be present in the samples containing the blended raw water sources.

The sources for the water investigated as part of this project are selected due to their contribution to the Toowoomba water supply (and hence, the potential for NOM to be problematic after treatment with chlorine from Mt Kynoch is directly applicable in these waters), and/or to exemplify the characteristics of surface water within the area.

3.2. Sampling Methodology

A water sample of 500mL is to be collected from each source on a weekly basis for a total of ten weeks. The water samples to be collected from the Mt Kynoch Water Treatment Plant will be collected from taps, which will be let run for a period of time before the sample is taken to ensure it is a representative sample. The sampling bottle will then be rinsed twice with the water before the sample is taken. The time at which it is taken will be noted. The water sample taken from the Japanese Gardens will be taken from the same designated location of the water body each week. The sampling bottle will be rinsed twice before the sample is taken and the time noted. The collection points for the sampling of each water source are shown in Figure 3-1.

Figure 3-1   **Points of collection for each of the water sources**

3.3. Analytical Measurements

To address the aim of monitoring the amount of natural organic matter in Toowoomba water sources and to determine the characteristics of the water, tests are to be carried out to measure NOM-related parameters of each of the water sources. Some of these water quality parameters are those that are also important for compliance with the US EPA's treatment technique requirement of the DBPR. This will be completed for a ten week period on a weekly basis when the water samples are collected. To obtain consistent and accurate results, the methods described by *Standard Methods For The Examination Of Water & Wastewater* 2005) will be followed, which is the recommendation made by the publication 'Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual' (Agency 1999). Each of the tests which are to be completed is explained in detail in the following sections.

3.3.1. pH

The pH is a measurement of how acidic or basic a solution is. It is defined as the negative logarithm of the hydrogen ion activity in moles per litre (*Standard Methods For The Examination Of Water & Wastewater* 2005). The pH range is from 0 to 14, with the most acidic solutions having a low pH value and becoming less acidic to a neutral pH value of 7 and then becoming more basic as pH increases from there. A pH meter is used for the purpose of this measurement.

Procedure

1. Remove electrodes from storage solution.
2. Rinse thoroughly with distilled water.
3. Blot dry with paper towel.
4. Immerse electrodes in a sample of the water source in a small beaker.
5. Gently stir the water with the electrodes until the ready symbol is seen.
6. Record the reading of pH and temperature.
7. Repeat steps 2-6 for each of the water sources.

3.3.2. Turbidity

Turbidity is an indication of the clarity of water, or how clear it is. This can be seen upon observation of the water but quantitative results are given by the actual measurement. This measurement is the measurement of the intensity of light scattered by the water sample (*Standard Methods For The Examination Of Water & Wastewater* 2005). As a water sample becomes less transparent, the higher the turbidity becomes as the intensity of the scattered light increases. A turbidimeter is used for the measurement and the units of measurement are nephelometric turbidity units (NTU). The turbidity of each of the water samples should be determined as soon as possible after collection for best results.

Procedure

1. Agitate the water sample.
2. Pour the water sample into the turbidity vial.
3. Wipe the outside of the vial to ensure it is free of any contaminants.
4. Place the vial into the turbidimeter with the lid paced on top.
5. Take the measurement by pressing the 'Read' button.
6. Record the reading.
7. Repeat steps 1-6 three times for each of the water sources tested.

3.3.3. Conductivity

The measurement of conductivity quantifies the ability of a solution to carry an electric current depending on the presence, concentration, mobility and valence of ions (*Standard Methods For The Examination Of Water & Wastewater* 2005). A solution is said to be a better conductor, the higher its conductivity. A conductivity meter is used for the measurement and gives the results in units of micro-Siemens.

Procedure

1. Rinse thoroughly with distilled water.
2. Blot dry with paper towel.
3. Immerse electrode in a sample of the water source in a small beaker.
4. Gently stir the water with the electrode until the ready symbol is seen.
5. Record the reading.
6. Repeat steps 2-6 for each of the water sources.

3.3.4. Total Dissolved Solids

The measurement of conductivity is useful in estimating the total dissolved solids in a water sample (*Standard Methods For The Examination Of Water & Wastewater* 2005). The same method and instrumentation is implemented as for the measurement of the conductivity. The conductivity meter is used to give the measurement in parts per million (ppm).

Procedure

1. After the conductivity measurement is taken, leave the electrode immersed in the sample and change the mode of the measurement device to measure TDS.
2. Gently stir the water with the electrode until the ready symbol is seen.
3. Record the reading.
4. Repeat steps 1-3 for each of the water sources.

3.3.5. Alkalinity

The measurement of alkalinity determines the acid-neutralizing capacity of a water (*Standard Methods For The Examination Of Water & Wastewater* 2005). A potentiometric titration to a preselected pH is completed. A pH value of 4.3 was selected as the end-point due to estimating the total alkalinity concentration as 500 milligrams of calcium carbonate ($CaCO_3$) per litre as per suggested (*Standard Methods For The Examination Of Water & Wastewater* 2005). Alkalinity varies with the selected end-point used and so this must be reported with the measurement. Hydrochloric acid is to be used in the titration and the amount of this added to the water sample to reach the preselected pH is used in the calculation of the alkalinity. Alkalinity is determined using the equation:

Alkalinity, mg $CaCO_3$/L = (acid amount added * acid normality * 50,000) / mL sample.

Procedure

1. Prepare 0.1N hydrochloric acid solution.
2. Pour a water sample into a beaker.
3. Gently mix the water sample with a magnetic stirring rod and electronic mixing equipment.
4. Immerse the probe of the pH meter in the water sample.
5. Record the initial pH.
6. Add acid to the water sample in small increments. Smaller additions of acid are made as the end-point is approached until pH equilibrium is achieved at this endpoint.
7. Record the amount of acid added to reach this pH, with the final pH.
8. Calculate the alkalinity using this amount of acid that was added.

3.3.6. Dissolved Organic Carbon

The measurement of dissolved organic carbon (DOC) is the value used to indicate the concentration of the organic matter present in the water sample. 'For drinking waters in particular, organic compounds may react with disinfectants to produce potentially toxic and carcinogenic compounds' (*Standard Methods For The Examination Of Water & Wastewater* 2005) which is the phenomenon being investigated in this project and the particular reason the amount of organic carbon in the water samples is being measured.

The total organic carbon (TOC) is defined as 'all carbon atoms covalently bonded in organic molecules' (*Standard Methods For The Examination Of Water & Wastewater* 2005). However as it is the DOC being measured, the water sample is first filtered through a 0.45μm pore diameter filter and it is the remaining fraction of organic carbon that is measured. The apparatus used for the measurement is a total organic carbon analyser which utilises the high-temperature combustion method. This method determines the quantity of organically bound carbon by breaking down the organic molecules and converting them to a single molecular form that can be measured quantitatively (*Standard Methods For The Examination Of Water & Wastewater* 2005).

Inorganic carbonates are converted to carbon dioxide with acid and then are removed by purging. Then a portion of the water sample is injected into a heated reaction chamber with an oxidative catalyst. The water is vaporized and converted to carbon dioxide and H_2O. The carbon dioxide is transferred with a carrier gas to be measured by a nondispersive infrared analyser (*Standard Methods For The Examination Of Water & Wastewater* 2005). This method therefore actually measures the fraction of total organic carbon that is not removed by the gas stripping process, or the nonpurgeable organic carbon (NPOC). 'In many surface and ground waters the purgeable organic carbon contribution to TOC is negligible. Therefore, in practice, the nonpurgeable organic carbon determination is substituted for TOC' (*Standard Methods For The Examination Of Water & Wastewater* 2005).

Procedure

1. Filter the water sample through a 0.45μm pore diameter filter into a vial.
2. If the sample is to be stored before measurement, place a lid on the vial and store the sample in the refrigerator.
3. Place the water samples, with additional standard samples, in the TOC Analyser machine for measurement.
4. Set up the machine for measurement.
5. Record the readings once the testing has completed.

3.3.7. Ultraviolet Absorption

UV absorption is a useful surrogate measure of selected organic constituents commonly found in water such as lignin, tannin, humic substances which strongly absorb ultraviolet (UV) radiation. 'Strong correlations may exist between UV absorption and organic carbon content, colour, and precursors of trihalomethanes (THMs) and other disinfection by-products' (*Standard Methods For The Examination Of Water & Wastewater* 2005). UV light is absorbed in a water sample in proportion to the concentration of the UV-absorbing organic constituents present in the sample. Typically, natural organic matter has an absorption profile which exhibits a curve with increasing absorption with decreasing wavelength. The method utilised for the measurement of UV absorption is intended to provide an indication of the total concentration of UV-absorbing organic constituents, rather than to detect certain individual constituents. A spectrophotometer is used for the measurement of the UV absorption, which has the units of cm^{-1}. The measurement procedure includes filtering the water sample to control variations in the absorption caused by particles. The UV absorption is to be measured over a range of wavelengths from 190 nm to 750 nm. This produces an absorption profile but the wavelength of particular interest will be 254 nm, historically used as the standard wavelength. 'Specific absorption, the ratio of UV absorption to organic carbon concentration, has been used to characterize natural organic matter' (*Standard Methods For The Examination Of Water & Wastewater* 2005). This calculation is therefore intended to be included in the analysis of the results from the measurements of the UV absorption and DOC concentration.

Procedure

1. Filter a portion of the water sample through a 0.45μm pore diameter filter.
2. Turn on the spectrophotometer and set it up for measurement.
3. Scan a sample of distilled water to provide the baseline for the measurement.
4. Pour the water sample into the vial to be used for testing.
5. Wipe clean the outside of the vial.
6. Measure the UV absorbance of the water sample by pressing scan when the sample is in place in the spectrophotometer.
7. Repeat steps 4-6 for each of the water samples.

3.3.8. Iron

The purpose of the measurement of the iron concentration in the water samples is to characterise the matter in the water. The direct air-acetylene flame method is used by the atomic absorption spectrometer apparatus. The method includes the water sample being aspirated into a flame and then atomized. Using a light beam that travels through this flame into a monochromator, the amount of light absorbed by the atomized element (which in this case is iron) is measured by a detector when the light beam reaches it. 'The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample' (*Standard Methods For The Examination Of Water & Wastewater* 2005). The results obtained are given as a concentration in the units of parts per million (ppm).

Procedure

1. Filter 50mL of the water sample through a 0.45μm pore diameter filter.
2. Acidify the water sample to pH<2 with 6N HNO_3.
3. Place the water samples, with additional standard samples, into the atomic absorption spectrometer.
4. Set up the machine for measurement.
5. Record the results once the testing has completed.

3.3.9. Anions

The measurement of the concentrations of the particular anions of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate is to be conducted in order to identify the type of matter present in the water samples. Ion chromatography is used to obtain these measurements utilising chemical suppression of eluent conductivity with an Ion Chromatography System ICS 2000. A water sample is passed through a series of ion exchangers and the anions 'are separated on the basis of their relative affinities for a low-capacity, strongly basic anion exchanger' (*Standard Methods For The Examination Of Water & Wastewater* 2005). The separated anions are directed through a suppressor device where they are converted to their highly conductive acid forms, which are

measured by conductivity (*Standard Methods For The Examination Of Water & Wastewater* 2005). The results obtained give the anion measurements as a concentration in the units of mg/L.

Procedure

1. Filter 5mL of the water sample through a 0.45μm pore diameter filter.
2. Place the water samples, with additional standard samples, into the ion chromatograph.
3. Set up the machine for measurement.
4. Record the results once the testing has completed.

3.4. Jar Testing

Jar testing will be the experimental procedure of choice to investigate the removal of the organic matter from the candidate water source. This process will simulate the effect of enhanced coagulation by adding an increased dose of coagulant and enabling the mixing and flocculation processes. The coagulant used in the experimentation will be aluminium sulphate (alum). The jar test involves dosing beakers of a 1L water sample with varying amounts of coagulant, rapid mixing, a gentle mixing process, and then the sample is allowed to sit to enable flocs to form (Yoong n.d.).

Jar testing will be conducted using the method outlined by the United States Environmental Protection Agency (US EPA), which states standard dosages to be strictly followed and used in the testing. The purpose of this testing is to determine the optimum dosage required to achieve maximum organic matter removal. The experimental set-up of the jar test is shown in Figure 3-2.

Procedure

1. Prepare coagulant solution by diluting the coagulant to result in a desired concentration. Specifically, dilute 10g of $Al_2(SO_4)_3.18H_2O_2$ in 1L of deionised water.
2. Collect 20 litres of raw water for the testing. If the collected water is not used immediately, refrigerate the sample and then ensure it is at room temperature again before testing.
3. Measure the pH and alkalinity of the raw water sample.
4. Determine how the pH changes with addition of coagulant, by placing a 1L water sample on a magnetic stirrer. Add alum in 10 mg/L increments. Measure and record the pH after each incremental coagulant dose.
5. Measure 1L of sample into 10 mixing jars and place the jars on the jar test apparatus.

6. Add coagulant dosages to each jar in 10mg/L increments from 10mg/L to 100mg/L.
7. Rapid mix at 100rpm for one minute.
8. Flocculate at 30rpm for 30 minutes.
9. Allow the jars to settle for 60 minutes.
10. Take samples with a pipette (with the tip being approximately 3cm below the water surface) from each jar for the measurement of turbidity. Measure the turbidity of each of the jars and the raw water sample.
11. Withdraw and filter additional samples for the measurement of DOC and alum residual. Measure the DOC for each of the jars and the raw water sample. Measure the alum residual for each of the jars.
12. Repeat steps 2-11 twice for each water source.

Figure 3-2   **Jar testing experimental set-up**

3.5. Trihalomethane Formation Potential Testing

Trihalomethane Formation Potential (THMFP) measurements are normally applied to evaluate the tendency of aquatic carbon to form disinfection by-products when treating it with chlorine. The measurements involve the water sample being buffered at pH 7.0, chlorinated with an excess of free chlorine, and incubated for a period of 7 days at approximately 25°C. The aim is to have a free chlorine residual of 3 to 5 mg/L at the end of this reaction time. Both the raw, untreated water from each source and the water treated with optimum alum doses will be tested for their potential to form DBPs. The unit of THMFP measurement is parts per billion (ppb) as chloroform ($CHCl_3$).

Procedure

1. Filter both treated and untreated water samples through 11 μm filter paper.
2. Prepare chlorine dosing solution by the dilution and titration of a 10-15% sodium hypochlorite solution.
3. Calculate the 7-day sample chlorine demand. This requires determining the initial chlorine concentration by titration and the chlorine residual by the chlorination and storage of the sample.
4. Chlorinate each of the water samples by adding to them a volume of chlorine determined in Step 3 in a 125mL amber bottle.
5. Incubate at 25°C in the dark for 7 days.
6. After the 7-day reaction period, remove the samples and prepare 10mL samples of each. Also, prepare a blank sample.
7. Add three drops of THM Plus Reagent 1 to each sample and place the lid on securely.
8. Gently swirl each sample to mix.
9. Add 3mL of THM Plus Reagent 2 to each sample, secure the lid and mix by shaking.
10. Heat the samples by placing them in a hot water bath while it is boiling for 5 minutes.
11. Remove the samples and cool them by placing them in a cool water bath for 3 minutes.
12. Add 1mL of THM Plus Reagent 3 to each sample.
13. Cool the samples again by placing them in a cool water bath for another 3 minutes.
14. To each sample, add the contents of the THM Plus Reagent 4 Powder Pillow.
15. Secure the lids of each sample and mix by shaking until the powder dissolves.
16. Wait 15 minutes.
17. Place the samples in the spectrophotometer and press 'Read' to take the measurements.

3.6. Chapter Summary

This chapter identified and explained the experimental methodologies implemented for this dissertation, including the collection of water samples, a number of analytical measurements, jar testing and trihalomethane formation potential testing.

Chapter 4 Monitoring Process Results and Analysis

This chapter will present, discuss and analyse the results obtained from the ten-week monitoring period. The numerical average results calculated for each of the analytical measurements are discussed. These are then compared to the results obtained for other water sources from previous research. The weekly analytical measurements for each water source are shown in plots to demonstrate the patterns and trends which occurred over the ten weeks. A comparison is made between these trends and that of the rainfall data for the same period.

4.1. Numerical Results

The measurements of pH, conductivity, total dissolved solids, turbidity, alkalinity, dissolved organic carbon, UV_{254} absorption, SUVA, iron and certain anions were taken over the ten-week period each week for each of the four water sources. This resulted in ten characteristic measurements for each water source, which were used to obtain an average value for each for each water source (as presented in Table 4-1) and plotted to show the graphical trend of the significant NOM characteristics (as seen in Figures 4-1 to 4-6).

Table 4-1   **Average values obtained over the 10 week monitoring period**

	Japanese Gardens	Cooby Dam	Perseverance Dam	Mt Kynoch Mixture
pH	7.778	7.977	7.264	7.204
Conductivity (μS)	224.7	730.0	260.9	269.9
Total Dissolved Solids (ppm)	112.3	365.2	130.6	135.0
Turbidity (NTU)	20.12	3.103	2.131	5.131
Alkalinity (mg $CaCO_3$ /L)	35.63	113.8	75.19	76.21
Dissolved Organic Carbon (mg/L)	4.511	7.289	5.749	5.260
UV_{254} Absorption (cm^{-1})	0.105	0.106	0.116	0.110
SUVA (L/mg-m)	2.394	1.516	2.115	2.171

From Table 4-1 it can be seen, all four water sources have an average pH within the range of 7.0 – 8.0, which is slightly basic but within the normal pH range of 6.5 – 8.5 for surface waters. Cooby Dam is seen to have conductivity and total dissolved solids measurements of more than twice that of the water sources. These measurements are not considered significant NOM characteristics and so no further analysis was completed for these values.

The turbidity results reflect a wide variance between that of the Japanese Gardens and the other water sources. The water sourced from the Japanese Gardens recorded a high turbidity of approximately 20 NTU, while the other water sources recorded values between 2 and 5 NTU.

The alkalinity values measured for each of the water sources are within a wide range with the Japanese Gardens measuring the lowest alkalinity value of approximately 36 mg $CaCO_3$/L; both the raw water mixture from Mt Kynoch and Perseverance Dam having similar measurements of 75 and 76 mg $CaCO_3$/L; and Cooby Dam recording the highest alkalinity value of 114 mg $CaCO_3$/L. Alkalinity is considered a very significant NOM characteristic. This value has a direct relationship with the ease of removal of the organic carbon from the water. There is a tendency for the removal of TOC to become more difficult as alkalinity increases and TOC simultaneously decreases (Agency 1999). It is therefore probable that it will be most difficult to remove the organic carbon from the Cooby Dam water due to it having the highest alkalinity of the four water sources.

The dissolved organic carbon measurements give a direct indication of how much organic matter is in the water sources and could therefore be considered the most pertinent measurements in addressing the aim of this project. The average DOC concentrations over the ten-week monitoring period were calculated as: 4.5 mg/L for the Japanese Gardens; 7.3 mg/L for Cooby Dam; 5.7 mg/L for Perseverance Dam; and 5.3 mg/L for the raw water mixture from Mt Kynoch. Each of these average concentrations is greater than the 2.0 mg/L which is used in the United States as the trigger for the implementation of the treatment technique (Agency 1999). This indicates the amount of organic carbon in the water sources exceeds that which can be considered acceptable for conventional treatment, according to the requirements in place in the United States, and in the absence of any Australian requirements, it is recommended that further treatment is necessary for these water sources to target the removal of organic carbon. The DOC concentrations of the Toowoomba water sources fall within the range of 4-8 mg/L. From this, together with the measured alkalinities, the required removal of TOC by enhanced coagulation as per the removal criteria in the United States can be determined. The percentage of TOC required to be removed from the water sources to ensure compliance with the US EPA regulations is 45 percent for the water of the Japanese Gardens and 35 percent for the other three water sources. It is acknowledged these regulations are in place for waters being treated for consumption purposes and the Japanese Gardens is not a water source used for these purposes. However, the same analysis is conducted for this water source as the others for the purpose of this project.

The average values of the UV_{254} absorption are not of particular importance. These results are more significant when plotted with time to demonstrate a trend or pattern, as discussed and seen later in Figure 4-5.

The SUVA values are calculated by dividing the measured UV_{254} absorption by the DOC concentration. The average SUVA values calculated for the four water sources are relatively low, ranging from 1.5 to 2.4 L/mg-m. SUVA gives an indication of the nature of the organic matter and will be further discussed upon the analysis of the plot of SUVA values in Figure 4-6.

The results for the iron and anion measurements are too detailed to be included here and so are omitted here but can be seen in the Appendix C. It is not necessary to inspect the specific values. These measurements were used to determine if the iron and anions in the water sources are likely to interfere with the UV absorption measurements. It can be concluded they should not cause any interference as their concentrations do not exceed the minimum detection limits in UV measurements. 'The minimum detection limit of chloride in UV measurements is 500 mg/L' (Al-Juboori et al. 2014) which is higher than the concentrations of chloride measured in the water samples. The concentrations of bromide were below the detection level of 14 µg/L. The concentrations of iron were not above 0.5 mg/L and the concentrations of nitrate did not exceed 5 mg/L. The concentrations for the other anions were considered too low to cause any interference as well.

4.2. Comparison with Other Studies

These average values can be compared to those obtained for other water sources in similar studies to determine which water sources have similar characteristics and therefore, may be treated in a similar manner. The waters for which a comparison can be made are the Turkish water studied by Ciner and Ozer (2013), the water of Iran studied by Bahman Ramavandi (2015) and the four South Australian or Victorian reservoirs studied by Chow et al. (2009). The measured characteristics of these waters from their respective studies were presented in Chapter 2.

The international water sources do not compare well with the water sources from Toowoomba. The Turkish water measured higher pH and alkalinity values but lower DOC concentrations than the Toowoomba waters. The Iranian water provided a slightly better comparison with similar pH values and a similar alkalinity to that of Cooby Dam. However, there are not enough similarities to make a valid comparison. Additionally, the study in Iran investigated the one Dez River water source over the change in seasons. The Australian reservoirs provide a better comparison to the Toowoomba waters than the overseas water sources. The reservoirs of Hope Valley, Myponga, Moorabool and Mt Zero have similar pH values and relatively similar turbidity and alkalinity values to those measured for the waters of Toowoomba. However, the characteristics of the waters are not similar enough, especially in regard to the DOC

concentrations, to draw the same conclusions for the water sources. This highlights the need for water sources to be treated on an individual location basis (instead of relying on assumptions or comparisons with other separate water sources).

4.3. Plots of the Measurements

The measurement of pH for each of the water sources over the ten-week monitoring period was plotted and can be seen in Figure 4-1. All measurements are shown to be within the pH range of 7.0 to 9.0. There is little fluctuation (with the exception of some measurements for the water from the Japanese Gardens), with a particularly consistent pH between 7.0 and 7.5 for the waters of Perseverance Dam and the Mt Kynoch mixture. There is a close alignment of the measurements for these two water sources. This could be attributed to the water from Perseverance Dam contributing to a large proportion of the raw water mixture prior to treatment at Mt Kynoch, which often is the case. The water from Cooby Dam shows slightly more variance in a higher pH range of 7.5 to 9.0, with the inclusion of one possible outlier. It appears pH is a fairly constant measurement over time for each of the water sources, with the most fluctuation occurring in the Japanese Gardens water and the Cooby Dam water most often recording the highest pH value.
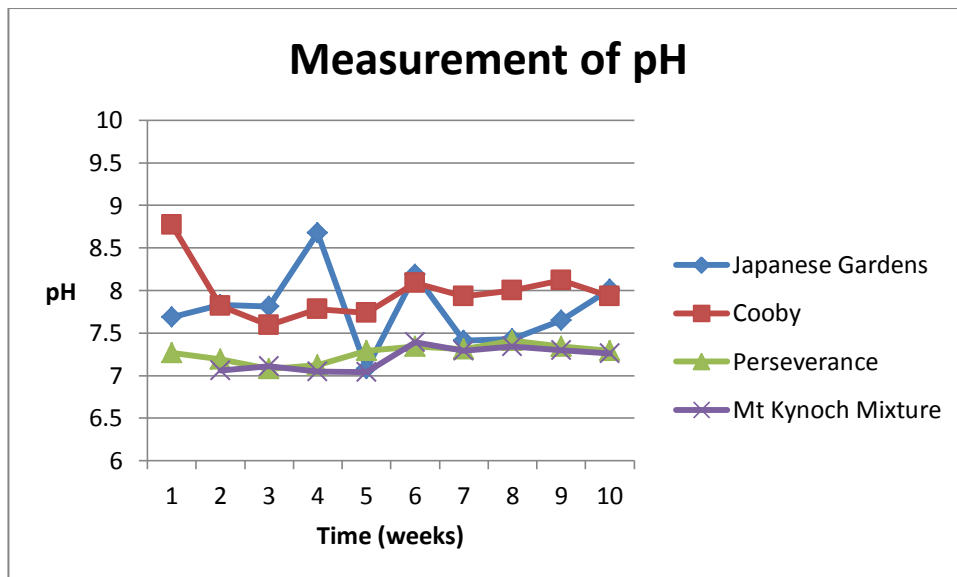
Figure 4-1   **pH measurements for the four water sources over the monitoring period**

It is clear from Figure 4-2 the water from the Japanese Gardens consistently had a much higher turbidity measurement than the other three water sources. While the turbidity values for the Japanese Gardens ranged from no less than 10 to greater than 35 NTU, none of the measurements for any of the other water sources ever exceeded 10 NTU. The turbidity of the Japanese Gardens water also fluctuated greatly within the monitoring period, as did the raw water mixture from Mt Kynoch. The waters from Cooby and Perseverance Dams remained fairly constant with one observed peak in turbidity each in the seventh and eighth weeks. These sources also consistently recorded

the lowest turbidity values. The removal of turbidity is the primary objective in conventional water treatment for consumption. The turbidity results do not indicate any potential problems in regards to this, as the drinking water sources have relatively low measurements of turbidity which can be removed effectively. The water from the Japanese Gardens is not used for drinking purposes and so the higher turbidity measurements do not pose a problem.
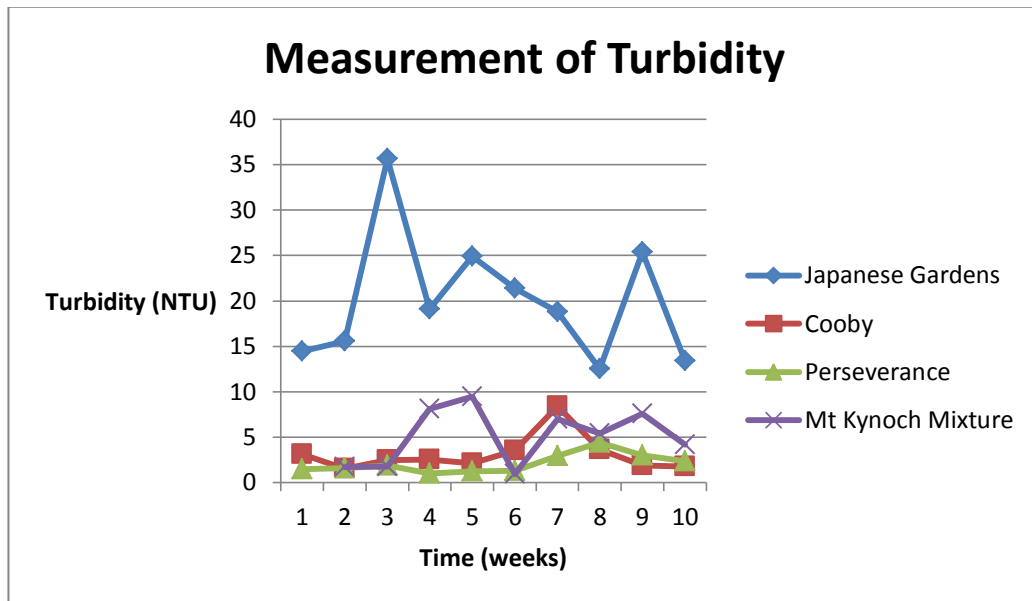
Figure 4-2   **Turbidity measurements for the four water sources over the monitoring period**

The alkalinity measurements for each of the water sources over the monitoring period were plotted and are shown in Figure 4-3. A very clear pattern is evident from the plot. Each water source has a fairly constant alkalinity measurement over the entirety of the monitoring period, with a peak in the second week. This could indicate the measurements for the second week represent an anomaly, where an error could have been made in taking these measurements. The measurements for the Japanese Gardens deviate from the pattern slightly, fluctuating marginally more than those of the other sources. The alkalinity measurements for the Perseverance Dam and Mt Kynoch water sources are consistently comparable. This close alignment is similar to that of the pH measurements, and so this could again be attributed to the water from Perseverance Dam contributing to a large proportion of the raw water mixture prior to treatment at Mt Kynoch. From Figure 4-3, there is also a very clear division between the numerical values of the measurements of each of the water sources. This allows the convenient comparison of the water sources. The water from the Japanese Gardens consistently measures the lowest alkalinity of the water sources by a considerable margin. The Cooby Dam water source consistently measures the highest alkalinity of the water sources. The comparable alkalinity measurements of Perseverance Dam and Mt Kynoch are between those of the other two water sources, with the same margin of difference between the lower values of the Japanese Gardens and the higher values of Cooby Dam. The evident trend of the measurements indicates alkalinity is a constant characteristic with time particular to a certain water source.
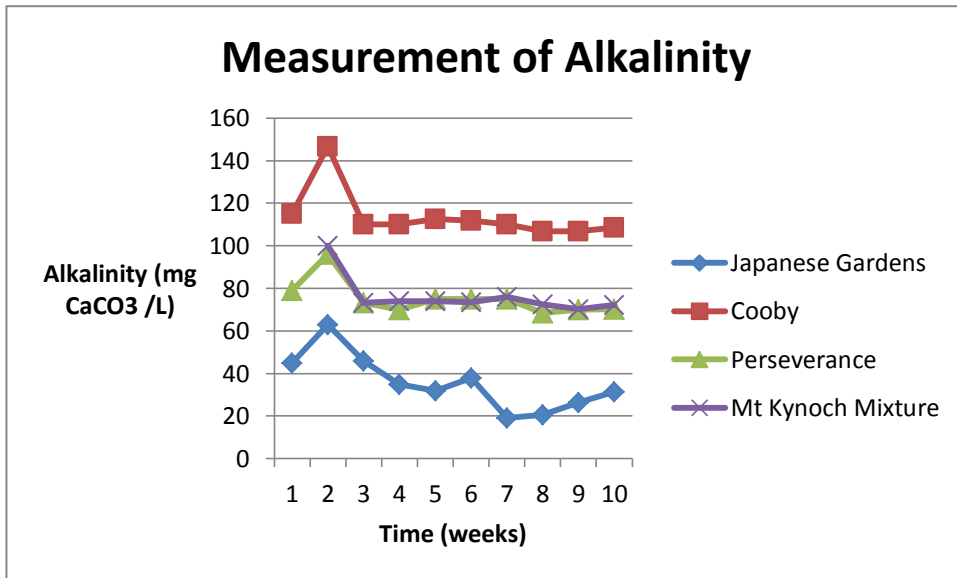
Figure 4-3 Alkalinity measurements for the four water sources over the monitoring period

The plot of the pertinent measurements of the DOC concentrations can be seen in Figure 4-4. These measurements give the direct indication of how much organic matter is in the water sources. The water from Cooby Dam consistently measures the greatest concentration of DOC within the range of 6.0 to 13.0 mg/L. The Japanese Gardens is seen to have the lowest DOC concentration within the range of 3.0 to 6.0 mg/L. Most of the measurements for the Perseverance Dam and Mt Kynoch water sources are between 4.0 and 6.0 mg/L, with the exception of one peak for each of the sources towards the end of the monitoring period in the ninth and tenth weeks. Peaks in the measurements can be observed for the Cooby Dam water in the seventh and ninth weeks. The water from the Japanese Gardens exhibits no sharp increases in the DOC concentration measurements. Instead a gradual increase to the maximum measurement in week six of the monitoring time period can be seen.

The results obtained for the purpose of this project were from measurements taken in a ten-week period from March to May in autumn. Observations and conclusions of how the concentrations change over time can only be made for this ten week period. Significantly different changes may occur over a longer period of time. Some waters exhibit seasonal changes in organic carbon concentrations due to algal activity or snow melts, for example (Agency 1999). Some changes can be rapid such as during storm events. Other source waters have a consistent concentration of organic carbon as a result of source water storage in reservoirs.

The most important observation that can be made is that all the DOC measurements within the ten weeks for each of the water sources are greater than the 2.0 mg/L that is used in the United States as the threshold above which further treatment in the form of enhanced coagulation must be implemented. In the United States a water treatment plant that practices conventional treatment of surface water must comply with EPA regulations and implement the treatment technique if the raw water has a TOC

concentration of greater than 2.0 mg/L (Agency 1999). Based on the results obtained for the purpose of this project, this is certainly the case for the water sources investigated that are utilised by the Mt Kynoch Water Treatment Plant. In the absence of any Australian requirements on this matter, it is recommended that further treatment is necessary for these water sources to target the removal of the excessive organic carbon present, in accordance with the regulations in place in the United States.
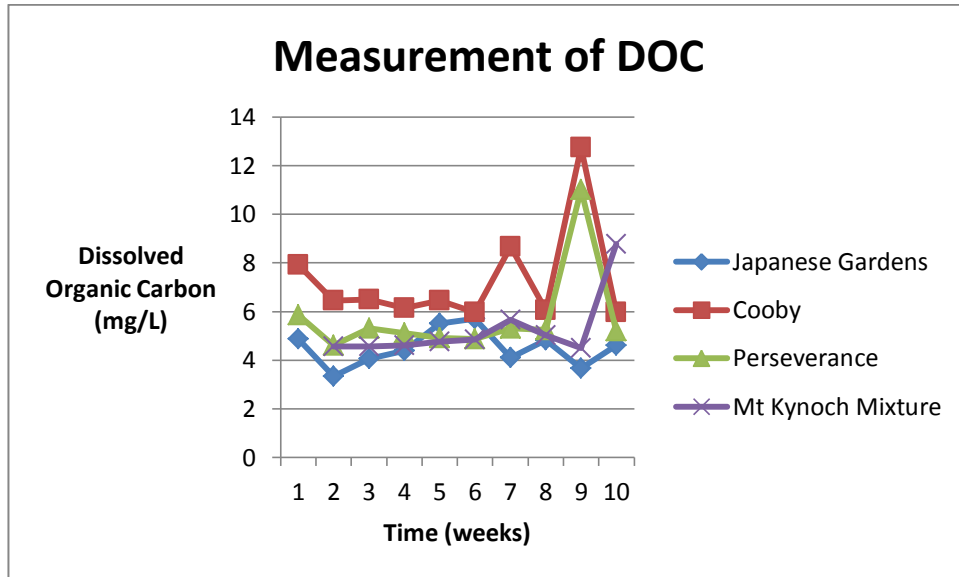
Figure 4-4   **Dissolved organic carbon measurements for the four water sources over the monitoring period**

The trend of the UV_{254} absorption measurements is demonstrated by the plot in Figure 4-5. It can be observed that the UV absorption is not a constant characteristic of a water source and fluctuates with time over the monitoring period. The measurements for each of the water sources follow a relatively similar trend to begin with and exhibit a sharp increase to a peak in the seventh week. The measurements for the waters of the Japanese Gardens and Cooby Dam then decrease significantly for the remainder of the monitoring period, whereas the other two water sources do not and remain fairly high. It appears the Japanese Gardens and Cooby Dam water sources show similar characteristics in regards to the UV_{254} measurements, as do Perseverance Dam and Mt Kynoch raw water mixture. Further analysis of the UV absorption was deemed to be outside the scope of this project.
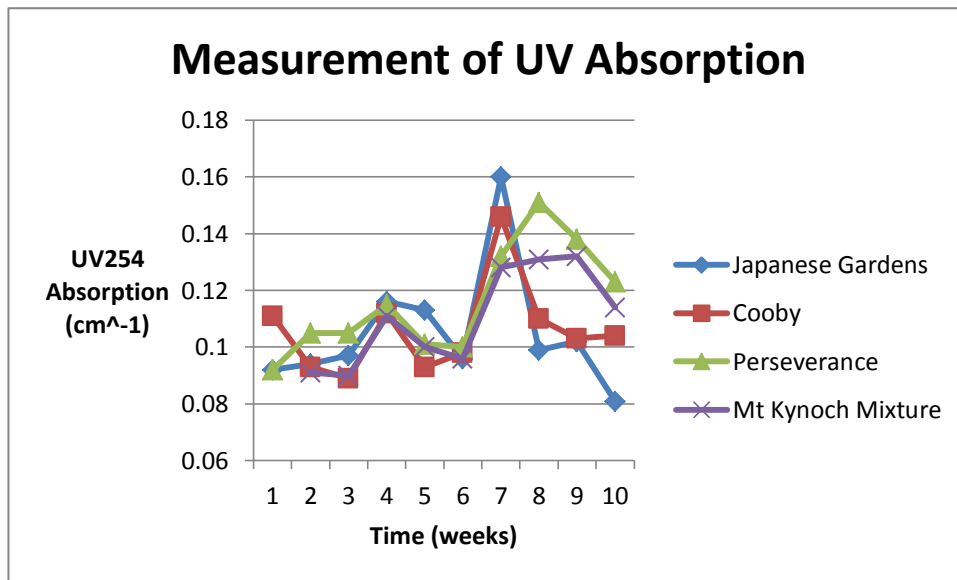
Figure 4-5 UV$_{254}$ Absorption measurements for the four water sources over the monitoring period

The SUVA values were calculated and plotted, as demonstrated by Figure 4-6. The values and trends of these measurements can be seen for the duration of the ten-week monitoring period. These values represent the ratio between the UV$_{254}$ absorption values and the DOC concentrations, which fluctuate during the monitoring period. The Cooby Dam water source tends to have the lowest SUVA values of the four water sources, with none of the measurements exceeding 2 L/ mg-m. The water sourced from Perseverance Dam and the Mt Kynoch raw water mixture have very similar results, ranging between 1.0 and 3.0 L/ mg-m. The measurements for the Japanese Gardens water cover a slightly greater range of higher values between 1.5 and 4.0 L/ mg-m.

SUVA is an indicator of the humic content of the water source 'The principle behind this measurement is that UV-absorbing constituents will absorb UV light in proportion to their concentration' (Agency 1999). Low SUVA values indicate a water source contains primarily non-humic organic matter and are not as responsive to enhanced coagulation. Waters with high SUVA values generally contain hydrophobic, humic organic matter (Yan et al. 2006) and are amenable to enhanced coagulation. Figure 4-7 describes further characteristics of a water source categorised into certain ranges of SUVA values.

Based on the results obtained and the literature, the water sources could be described as having low SUVA values and containing non-humic substances as the primary constituents of organic matter. The SUVA values of the Cooby Dam water source do not exceed 2 L/mg-m, and it can be characterised by the first group listed in Figure 4-7. Having the lower SUVA values, the Cooby Dam water may also be less responsive to enhanced coagulation. The other water sources have SUVA values between 2.0 and 4.0 L/mg-m, falling into the second group listed in Figure 4-7. These water sources may therefore contain more humic material than the Cooby Dam water source and could be more responsive to enhanced coagulation.
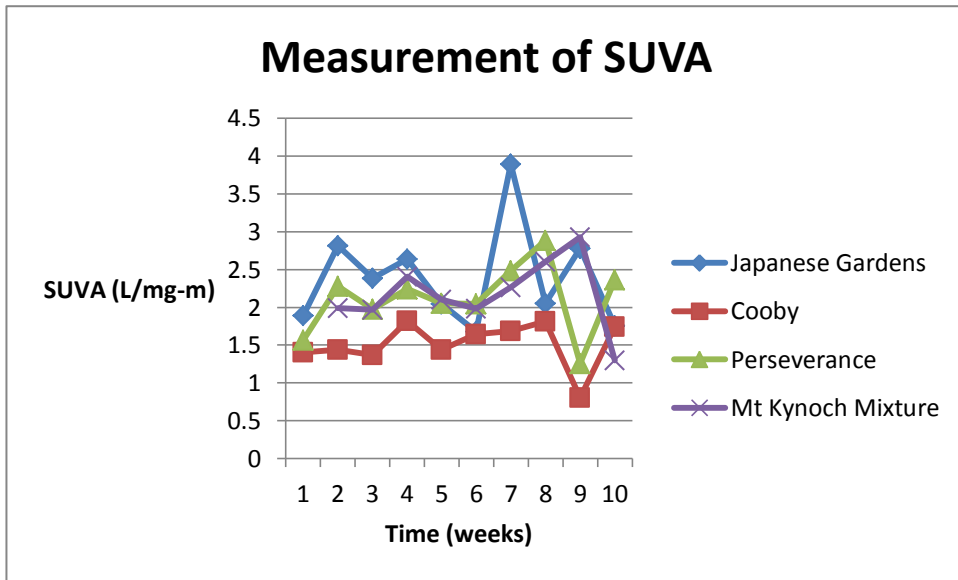
Figure 4-6   Calculated SUVA measurements for the four water sources over the monitoring period

SUVA	Composition	Coagulation	DOC Removals
< 2	Mostly Non-Humics Low Hydrophobicity Low molecular weight	NOM has little influence Poor DOC removals	< 25% for Alum Little greater for ferric
2 – 4	Mixture of Aquatic Humic and other NOM Mixture of Hydrophobic and Hydrophilic NOM Mixture of Molecular Weights	NOM influences DOC removal should be fair to good	25-50% for Alum Little greater for ferric
> 4	Mostly Aquatic Humics High Hydrophobicity High Molecular weight	NOM control Good DOC removals	50% for Alum Little greater for ferric

Figure 4-7   Characteristics of a water source dependent upon the SUVA value (Garcia 2005)

4.4. Comparison with Rainfall Data

It was to be determined if the tendency could be explained by correlating the measured characteristics with rainfall data obtained from Bureau of Meteorology. The aim is to determine whether the trends of the water characteristic measurements can be attributed to the amount of rainfall for that week.

Rainfall data for the same time period that the water monitoring took place was obtained from the Bureau of Meteorology, for locations closest to the locations from which the water samples were collected. The rainfall at the Cooby Creek Dam station was obtained for comparison with the water sourced from Cooby Dam. The Pechey Forestry station provided rainfall estimates for the area of the Perseverance and Cressbrook Dams. The Middle Ridge station was the closest rainfall station to the Japanese Gardens, and so that data was used for comparison to that water source. The rainfall measured at Mt Kynoch was also obtained for comparison. All locations revealed a very similar rainfall pattern over the investigated time period, as can be observed in Figure 4-7, and so it is not crucial which rainfall data is compared to which water source. The total rainfall was calculated from daily rainfalls for the week leading up to the day on which the water samples were collected and measured. It is not the numerical quantities of rainfall that are being analysed but rather the observed peaks and overall pattern.

Upon comparison of the trends evident in Figures 4-1 to 4-6 and those evident in Figure 4-7, there is no clear, consistent correlation between the measured NOM characteristics of the water and the amount of rainfall. The measurements of pH and alkalinity are fairly regular throughout the entire time period, with few exceptions, and so it is apparent these characteristics are unlikely to be affected by the rainfall. The measurements of turbidity, DOC, UV absorption and SUVA show a slightly more similar trend to that of the rainfall with observed fluctuations sometimes correlating with that of the rainfall. However, this is not consistent and there appears to be no direct correlation, even when accounting for the direct, immediate effect of the rainfall as well as the rainfall runoff which would have a delayed effect. For example, the measurements of turbidity do show fluctuations for each water source but these do not appear to mirror the rainfall patterns. Some of the higher turbidity measurements do correspond with some of the peaks of rainfall for some of the water sources but this is not consistent for any water source or for particular peaks of rainfall. The other measurements, particularly the UV absorption, show slightly more favourable results to indicate a correlation with rainfall but there is not enough evidence this pattern is a direct link and not coincidental.

The tendency of the water characteristic measurements cannot be conclusively explained by the rainfall based on the findings of this project. It may have some effect on the water characteristics but it is clearly not the only influence on these measurements, indicating other factors are in effect too, particularly for the cases of the pH and alkalinity measurements. The effect of rainfall on the organic carbon concentrations should not be overlooked though. Increased organic carbon concentrations (and UV absorption values) after rainfall have been noted in the literature, specifically by Krasner (1999) as cited by Garcia (2005) and the CRC (n.d.).

It is recommended that further investigation into the effect of rainfall on NOM water characteristics for the Toowoomba water sources is to occur before any definitive conclusions are made. However, for the purpose of this project the water characteristic measurements do not demonstrate a clear, consistent correlation with the rainfall data.
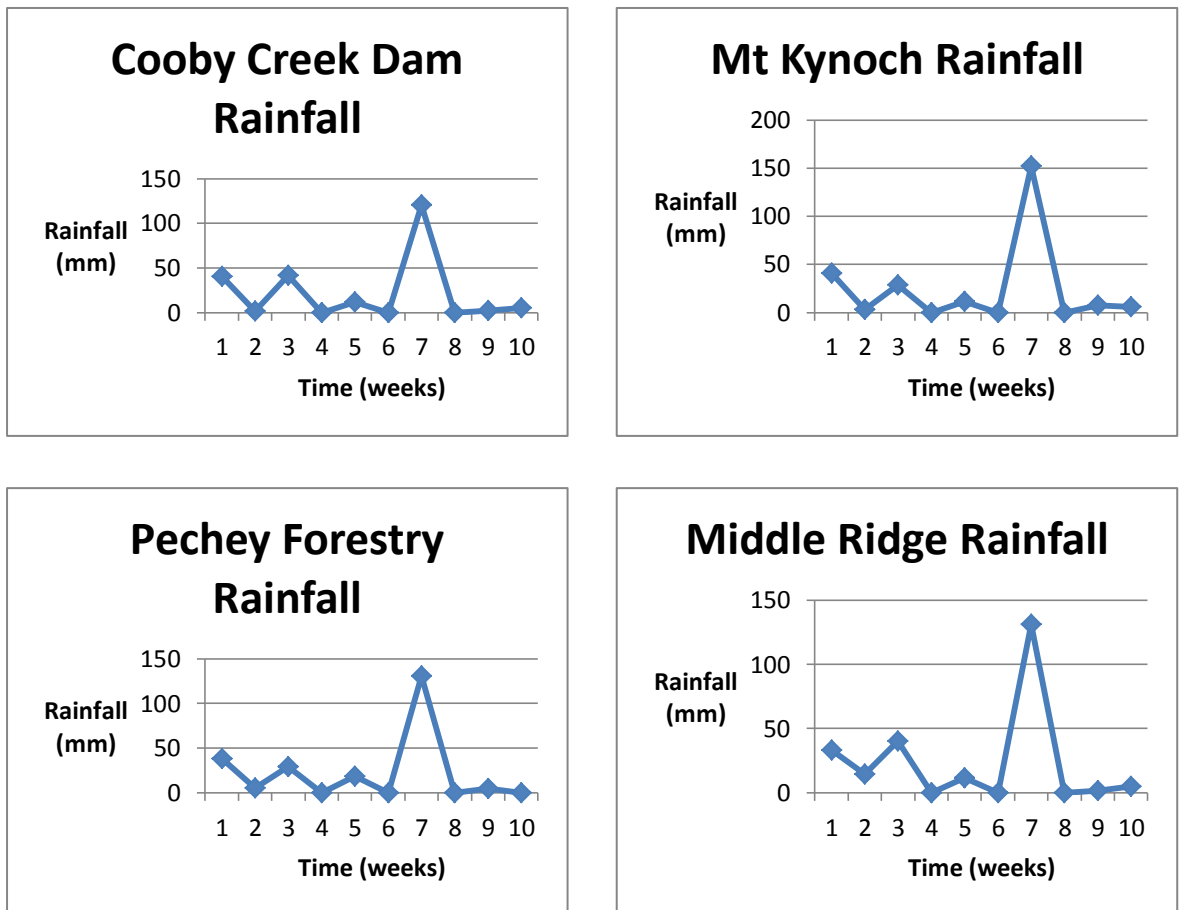
Figure 4-8   **Rainfall data for locations closest to water sampling locations for the same duration of time as the monitoring period (Meteorology 2015)**

4.5. Chapter Summary

The results and analysis presented in this chapter contribute to the characterisation of the water sources based upon the analytical measurements. The average numerical results provided quantifiable values whereas the plots of the weekly results identified trends that developed over the time period. The dissolved organic carbon concentration results are of particular importance for this study. Comparisons were made with the results from other studies regarding different water sources and rainfall data.

Chapter 5 Jar Testing Results and Analysis

This chapter presents and discusses the results and analysis from the investigation of the removal of organic carbon by enhanced coagulation. Bench-scale jar testing was completed for each of the four water sources, with alum as the coagulant in 10mg/L increments from 10mg/L to 100mg/L. The results obtained include the measurements of pH, initial raw water alkalinity, turbidity, DOC and residual alum. Results which were subsequently calculated included the incremental DOC removal, the DOC removal percentage and the incremental slope.

The optimum coagulant dose is to be determined by methods of analysis for the maximum removal of organic matter. A number of methods were utilised for this purpose. The optimum coagulant dose for the removal of turbidity is also considered, as this is of primary concern in practice in water treatment plants currently, to determine an optimum coagulant dose for the removal of both organic matter and turbidity.

Alum residual is also to be minimised when determining an optimum dose. However, the obtained results are considered unreasonable as there is no evident trend with increasing addition of alum. It is suspected the measurements were below the detection limit of the AAS machine. Therefore, the alum residual results are not considered in the analysis but still have been recorded in Tables 5-1 – 5-4. The low values of the results indicate residual alum will be minimal in each of the source waters with the addition of any of the alum doses and should not pose a problem. The Australian Drinking Water Guideline for aluminium is 0.2 mg/L (Council & Council 2011) and so even when this value is exceeded, it is only minimally exceeded and so should be resolved with further treatment processes in practice.

It should be noted the Perseverance Dam water source additionally contained water from Cressbrook Dam for the period of time that the experimental results were obtained for the purpose of jar testing.

5.1. Discussion of the Results

Two jar tests were completed using water samples sourced from the Japanese Gardens. The results from the first jar test have been disregarded due to the initial DOC measurement of the raw water sample considered to be an error. The single measurement was significantly greater than any DOC measurement taken previously for the water source. The initial value for the raw water is significant in allowing subsequent analysis to be made in reference to removal percentages, and so this cannot occur if this value is incorrect. The results were still recorded and included in the Appendix D for completion but are omitted from analysis. Consequently, three measurements were taken of the DOC of each of the raw water samples to minimise the risk of this occurring again.

The second jar test for the Japanese Gardens water had more reasonable results for the measurement of the organic carbon, with no values being considered anomalies. These results are documented in Table 5-1. Three measurements were taken of the DOC of the raw water to gain an average value, minimise the risk of another error occurring and to be able to more easily identify outlying data. This initial, average measurement of the DOC was 3.82mg/L for the raw water and this was reduced to a minimum of 2.195mg/L with the 80mg/L addition of alum.

Table 5-1   Jar testing results for the Japanese Gardens water

Alum Added (mg/L)	pH	Alkalinity (mg CaCO$_3$ / L)	DOC (mg/L)	Residual Alum
0	7.70	42.0	3.82	-
10	7.14	-	3.63	0.106
20	6.82	-	3.26	0.000
30	6.51	-	2.99	0.383
40	6.27	-	2.79	0.604
50	6.08	-	2.73	0.714
60	5.90	-	2.42	0.327
70	5.71	-	2.44	0.023
80	5.50	-	2.20	0.000
90	5.27	-	2.23	0.438
100	5.05	-	2.31	0.410

The jar test for the raw water mixture from Mt Kynoch gave DOC measurements with one apparent error for the 70mg/L dose of alum. This measurement does not follow the observed trend of decreasing organic carbon with increasing alum addition and the increase is too sharp to not be considered as an anomaly.   The jar testing enabled the DOC to be reduced to 3.493mg/L with the addition of 90mg/L of alum from 6.65mg/L present in the raw, untreated water. The results for the Mt Kynoch raw water mixture are shown in Table 5-2.

Table 5-2   Jar testing results for the Mt Kynoch raw water mixture

Alum Added (mg/L)	pH	Alkalinity (mg CaCO$_3$ / L)	DOC (mg/L)	Residual Alum
0	7.35	65.5	6.65	-
10	7.02	-	6.03	0.08
20	6.81	-	5.85	0.05
30	6.61	-	5.07	0.01
40	6.45	-	4.75	0.05
50	6.32	-	4.39	0.00
60	6.20	-	4.14	0.00
70	6.09	-	5.06	0.15
80	5.99	-	3.75	0.32
90	5.88	-	3.49	0.00
100	5.77	-	3.74	0.27

The DOC measurements from the jar tests of both the Perseverance and Cressbrook, and Cooby Dam waters both follow similar trends of decreasing organic carbon with increasing coagulant addition (as seen in Tables 5-3 and 5-4). The raw water from the Perseverance and Cressbrook dams measured a DOC concentration of 5.86mg/L and jar testing with an alum dose of 100mg/L decreased this to a minimum of 3.35mg/L. Greater DOC concentrations were measured for the water from Cooby Dam, which is consistent with the measurements obtained during the monitoring period. An initial value of 6.29mg/L was measured for the raw, untreated water and an alum dose of 90mg/L reduced this to a minimum of 4.276mg/L. For both sets of results, the DOC measurement for the 10mg/L alum addition is considered an anomaly. By following the apparent trend, it can be observed an error could have occurred with the DOC measurement for either the raw water sample or the 10mg/L alum addition. It was concluded the raw water sample measurements could not be anomalous as three separate measurements were taken to gain an average and all measurements were consistent. Therefore, the results for the 10mg/L addition of alum are considered irregularities.

Table 5-3   Jar testing results for the water from Perseverance and Cressbrook Dams

Alum Added (mg/L)	pH	Alkalinity (mg CaCO$_3$ / L)	DOC (mg/L)	Residual Alum
0	7.54	69.5	5.86	-
10	7.17	-	6.23	0.41
20	6.94	-	5.45	0.32
30	6.75	-	5.10	0.35
40	6.60	-	4.63	0.05
50	6.48	-	4.35	0.12
60	6.37	-	4.01	0.19
70	6.26	-	3.92	0.31
80	6.16	-	3.65	0.07
90	6.06	-	3.53	0.12
100	5.95	-	3.35	0.17

Table 5-4   Jar testing results for the Cooby Dam water

Alum Added (mg/L)	pH	Alkalinity (mg CaCO$_3$ / L)	DOC (mg/L)	Residual Alum
0	8.22	118.5	6.29	-
10	7.60	-	6.58	0.00
20	7.30	-	5.65	0.68
30	7.09	-	5.43	0.00
40	6.92	-	5.34	0.14
50	6.80	-	4.95	0.61
60	6.69	-	4.95	0.34
70	6.60	-	4.92	0.20
80	6.52	-	4.31	0.00
90	6.44	-	4.28	0.37
100	6.37	-	4.46	0.10

The results from each of the water sources follow the trend of coagulant dose efficiency for removal of DOC being initially high and then decreases at the higher doses. This is the expected trend of natural waters treated with an inorganic coagulant such as alum, and occurs as a result of the higher molecular weight hydrophobic compounds being removed and leaving smaller molecular weight hydrophilic compounds (J. van Leeuwen 2005).

5.2. Target pH

It is a requirement of the Step 2 procedure of the treatment technique in place in the United States 'that incremental coagulant addition be continued until the pH of the tested sample is at or below the "target pH" to ensure that the treatability of the sample is examined over a range of pH values. The target pH values are dependent upon the alkalinity of the raw water to account for the fact that higher coagulant dosages are needed to reduce pH in higher alkalinity waters' (Agency 1999). The target pH values are shown below in Table 5-5.

Table 5-5   Target pH values under Step 2 Requirements (Agency 1999)

ALKALINITY (mg/L as $CaCO_3$)	TARGET pH
0 – 60	5.5
>60 – 120	6.3
>120 – 240	7.0
>240	7.5

Therefore, the Japanese Gardens water with an alkalinity of 42 mg $CaCO_3$/L has a target pH of 5.5, and the other water sources each have a target pH of 6.3 with measured alkalinities within the range of 60-120 mg $CaCO_3$/L.

It was arbitrarily decided to test all four water sources with alum doses from 10mg/L up to 100mg/L in 10mg/L increments without pH adjustment. In doing so, the pH of the tested sample was lowered to the target pH for each of the water sources with the exception of the water from Cooby Dam.

The 8.22 pH of the raw water sampled from Cooby Dam (shown previously in Table 5-4) was lowered to 6.37 after the addition of 100mg/L of alum, narrowly not achieving the target pH. However, it was decided significant organic carbon removal was achieved with the selected range of coagulant dosages over a range of pH values.

The target pH of 5.5 was achieved by the addition of 80mg/L of alum to the water from the Japanese Gardens, which initially recorded a pH of 7.7. For waters such as the sample from the Japanese gardens with an alkalinity less than 60 mg $CaCO_3$/L, it is likely small amounts of coagulant will lower the pH below the target pH before significant organic carbon removal is able to occur, and so it is recommended that necessary chemicals be added to maintain a higher pH until more organic carbon is removed. The jar test was conducted without this pH adjustment because the target pH was achieved after the addition of 80mg/L of alum so only the jars with additions of

90mg/L and 100mg/L of alum would be affected, before which it was assumed significant organic carbon removal would have occurred. The measured pH results for the Japanese Gardens water can be seen in Table 5-1 with the DOC measurements.

Both the raw water mixture from Mt Kynoch and the water from Perseverance and Cressbrook Dams had a target pH of 6.3. This was achieved after the addition of 60mg/L of alum for the Mt Kynoch water, lowering the pH from 7.35. An alum dose of 70mg/L achieved the target pH for the Perseverance and Cressbrook water from an initial pH of 7.54. These results can be seen in Tables 5-2 and 5-3.

5.3. Analysis of the DOC Removal

5.3.1. US EPA Step 1 Requirements

The required organic carbon removal percentages for each of the source waters were previously determined from the results obtained from the 10-week monitoring period. The alkalinity and DOC measurements of the raw water collected for jar testing replicates the same conclusions for each of the water sources. To repeat, the water sampled from the Japanese Gardens requires 45% of the organic carbon to be removed to comply with the US EPA requirements. The three other source waters have a required removal percentage of 35% for compliance. Indicated by the results obtained, the water sourced from the Japanese Gardens and Cooby Dam did not achieve these removal percentages for the particular jar tests conducted. The water from the Japanese Gardens achieved a maximum DOC removal percentage of 42.5% when the 80mg/L dose of alum was added. The 35 percent removal requirement was not achieved by the Cooby Dam water as the most amount of DOC removed from the water was measured and recorded to be 31.99 percent with the addition of the 90mg/L dose of alum. The water sourced from Perseverance Dam and the raw water mixture from the Mt Kynoch Water Treatment Plant achieved organic carbon removal percentages which are in compliance with the US EPA requirements. Compliance was met for the water from Perseverance Dam when 37.8 percent of the organic carbon had been removed with an alum dose of 80mg/L. This occurred for the raw, Mt Kynoch mixture at an alum dose of 60mg/L to achieve 37.78 percent removal. A higher amount of organic carbon was measured for the 70mg/L dose of alum though, reducing the removal percentage to 23.9%. This can be considered an anomaly as the remaining jars had increasingly lower amounts of organic carbon recorded, with the exception of the last jar. This irregular result could be the result of an error occurring due to equipment contamination. Therefore, the 70mg/L dose of alum could be interpreted as the coagulant dose required for compliance if the following result is considered an anomaly and omitted from analysis. Alternatively, the 80mg/L dose of alum achieved a removal of 43.64 percent of organic carbon, with the remaining jars consistently recording removal percentages above the compliance percentage. The coagulant dose at which compliance is met is one method of analysis for determining the optimum coagulant dose.

5.3.2. Point-to-point Curve Method of Data Analysis

If a water source is unable to achieve the required removal percentage, an alternative percent of organic carbon removal requirement is established by conducting jar tests similar to the tests carried out for the purpose of this project. This alternative percent of organic carbon removal requirement is defined as the percent of organic carbon removal achieved at the point of diminishing return (PODR). The PODR is defined as 'the point on the TOC removal vs. coagulation addition plot where the slope changes from greater than 0.3/10 to less than 0.3/10, and remains less than 0.3/10 until the target pH is reached' (Agency 1999). This PODR can be determined by two methods of data analysis: the point-to-point curve and the continuous curve developed using regression techniques, to set the alternative organic carbon removal requirement. For the process of analysing the jar test results to set an alternative organic carbon removal requirement, 'the Step 2 TOC removal percentage is set at the last point (i.e. highest coagulant dose) on the TOC removal vs. coagulant dose plot where the magnitude of the slope is greater than or equal to 0.3 mg/L TOC removal per 10mg/L of alum' (Agency 1999). The literature states the organic carbon being removed as TOC. However, for the purpose of this project the organic carbon investigated was the DOC, and therefore these terms are used interchangeably with regards to the jar testing results analysis.

The point-to-point curve method of data analysis uses the alum doses and corresponding DOC measurements to calculate the incremental slope. The incremental slope between each point is calculated to allow a direct comparison with the PODR requirement slope by equation 5-1:

$$\text{Slope} = (TOC_2 - TOC_1)/(Dose_2 - Dose_1) \qquad\qquad (5\text{-}1)$$

where: TOC_1 = TOC level of first data point in mg/L
$\qquad$ TOC_2 = TOC level of second data point in mg/L
$\qquad$ $DOSE_1$ = Coagulant dose of first data point in mg/L
$\qquad$ $DOSE_2$ = Coagulant dose of second data point in mg/L (Agency 1999)

Analysis of this slope between each point then allows the PODR to be identified. It was the case for each of the source waters that the value of the slope between each point meant the PODR was met more than once. The results from the jar testing of each of the four source waters were analysed.

The removal of DOC with coagulant addition is documented in Table 5-6 for the water sourced from the Japanese Gardens. As can be seen, the slope of the point-to-point curve reaches -0.03 between the alum doses of 20 and 30 mg/L before falling below this value as a result of the addition of a higher alum dose. The slope falls back to -0.03 between the alum doses of 60 and 70 mg/L. Since the slope does not equal of fall below -0.03 beyond this point until the target pH is reached, this point is selected as the PODR and will set the alternative TOC removal percentage. The alternative TOC removal percentage is set at the second (higher) dose of 70mg/L. At a dose of 70mg/L, the DOC removal is calculated to be 36.18 percent, and this is the alternative removal percentage. This is shown graphically in Figure 5-1.

Table 5-6   Jar test results for the Japanese Gardens water for point-to-point curve data analysis

Alum Dose (mg/L)	Settled Water DOC (mg/L)	Incremental DOC Removal (mg/L)	Incremental Slope (mg-DOC/mg-Alum)	DOC Removal (%)
0	3.82	-	-	-
10	3.63	0.20	-0.020	5.108
20	3.26	0.37	-0.037	14.79
30	2.99	0.27	-0.027	21.85
40	2.79	0.20	-0.020	27.00
50	2.73	0.06	-0.006	28.62
60	2.42	0.31	-0.031	36.65
70	2.44	-0.02	0.002	36.18
80	2.20	0.25	-0.025	42.59
90	2.23	-0.04	0.004	41.57
100	2.31	-0.08	0.008	39.56
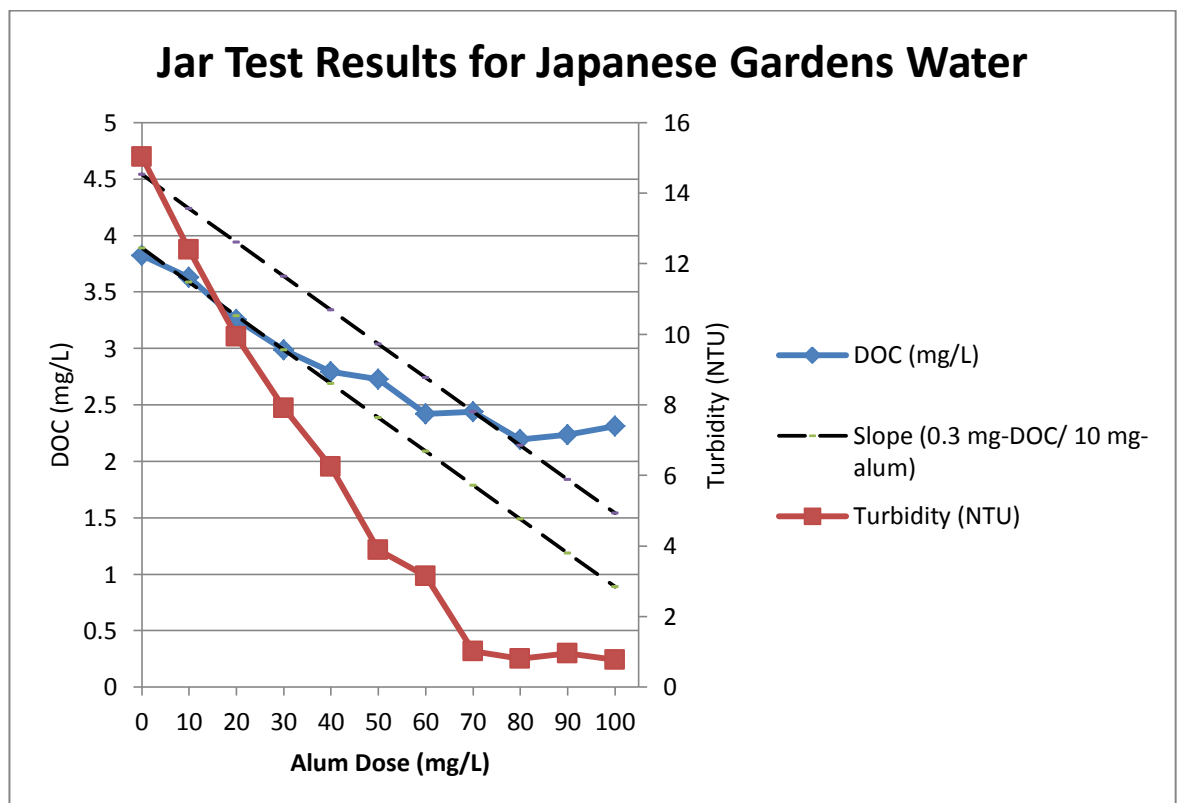
Figure 5-1   Point-to-point curve for determining the PODR for the Japanese Gardens water

As shown in Table 5-7, the slope of the point-to-point curve for the results of the Cooby Dam water reaches -0.03 between the alum doses of 20 and 30 mg/L. However, the slope below -0.03 further to the right on the curve at higher alum doses. This is shown graphically in Figure 5-2. The slope falls to -0.03 for the second time between the alum doses of 50 and 60 mg/L, and then again between 80 and 90 mg/L. Since the slope does

not equal or fall below -0.03 beyond this point (and the target pH is not reached by the alum doses tested), this point is the PODR and will set the alternative TOC removal percentage at the higher dose of 90 mg/L. At the alum dose of 90 mg/L the DOC removal is 31.99 percent which becomes the alternative removal percentage.

Table 5-7   Jar test results for the Cooby Dam water for point-to-point curve data analysis

Alum Dose (mg/L)	Settled Water DOC (mg/L)	Incremental DOC Removal (mg/L)	Incremental Slope (mg-DOC/mg-Alum)	DOC Removal (%)
0	6.29	-	-	-
10	6.58	-0.297	0.029	-4.719
20	5.65	0.931	-0.093	10.09
30	5.43	0.223	-0.022	13.64
40	5.34	0.093	-0.009	15.12
50	4.95	0.384	-0.038	21.22
60	4.95	0.008	-0.001	21.35
70	4.92	0.028	-0.0028	21.80
80	4.31	0.603	-0.060	31.39
90	4.28	0.038	-0.004	31.99
100	4.46	-0.186	0.019	29.03
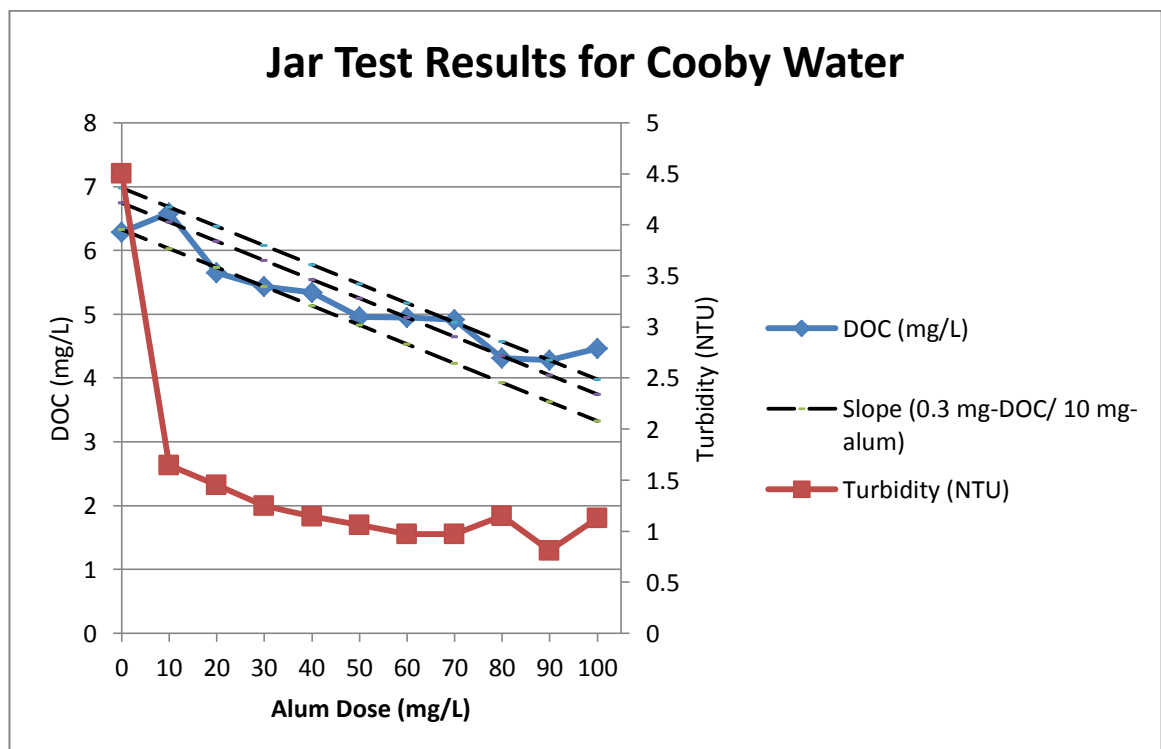
Figure 5-2   Point-to-point curve for determining the PODR for the Cooby Dam water

Table 5-8 documents the jar testing results for the water from the Perseverance and Cressbrook Dams. The slope between each of the points reaches -0.03 between the alum doses 40 and 50 mg/L. However, it falls below this value further to the right on the curve. This curve is shown graphically in Figure 5-3. The slope falls to -0.03 again between the alum doses of 60 and 70 mg/L. The slope does not equal or fall below -0.03 beyond this point, which is also the point at which the target pH is reached. Therefore, this point is selected as the PODR. The alternative TOC removal percentage is set at the dose of 70 mg/L, which has a DOC removal percentage of 33.13 percent.

Table 5-8   **Jar test results for the water from Perseverance and Cressbrook Dams for point-to-point curve data analysis**

Alum Dose (mg/L)	Settled Water DOC (mg/L)	Incremental DOC Removal (mg/L)	Incremental Slope (mg-DOC/mg-Alum)	DOC Removal (%)
0	5.86	-	-	-
10	6.23	-0.365	0.036	-6.221
20	5.45	0.775	-0.078	6.999
30	5.10	0.352	-0.035	13.00
40	4.63	0.468	-0.047	20.99
50	4.35	0.287	-0.029	25.88
60	4.01	0.339	-0.034	31.67
70	3.92	0.086	-0.009	33.13
80	3.65	0.274	-0.027	37.81
90	3.53	0.117	-0.012	39.80
100	3.35	0.179	-0.018	42.86
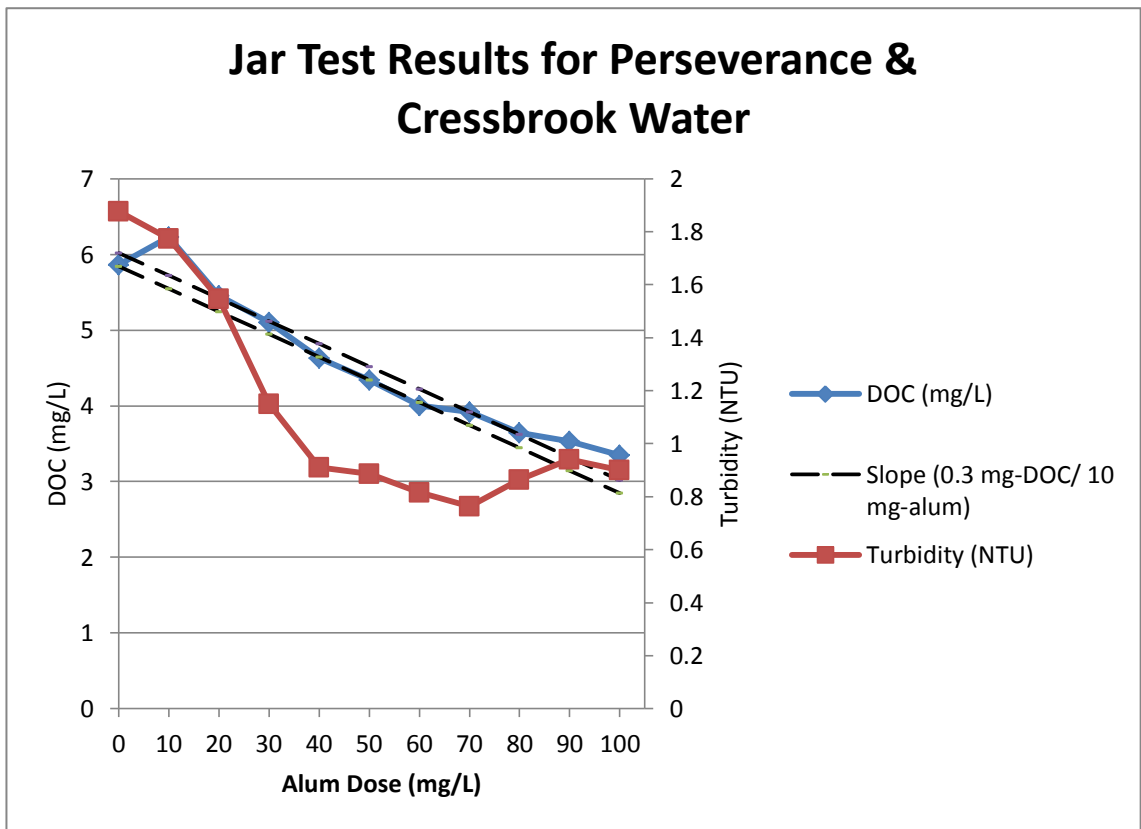
Figure 5-3 **Point-to-point curve for determining the PODR for the water of Perseverance and Cressbrook Dams**

The results from the jar testing of the Mt Kynoch raw water mixture used for this analysis are shown in Table 5-9. It can be identified that the slope of the point-to-point curve reaches -0.03 between the alum doses of 50 and 60 mg/L before the slope falls below this value again with further alum addition. The slope then reaches -0.03 again between the alum doses of 80 and 90 mg/L. Typically in this case, as seen by the other source waters, this second point where the PODR is met is selected. However, in this case the DOC measurement corresponding to the 70 mg/L alum dose has been identified potentially as an error. Omitting this point, the slope would remain more than -0.03. The target pH is also reached at the 60 mg/L dose and so analysis past this point is not necessary. Therefore, it is selected the alternative TOC removal percentage is set at 60 mg/L. The DOC removal percentage which occurs with this dose and becomes the alternative removal percentage is 37.78 percent.

Table 5-9   Jar test results for Mt Kynoch raw water mixture for point-to-point curve data analysis

Alum Dose (mg/L)	Settled Water DOC (mg/L)	Incremental DOC Removal (mg/L)	Incremental Slope (mg-DOC/mg-Alum)	DOC Removal (%)
0	6.65	-	-	-
10	6.03	0.619	-0.062	9.305
20	5.85	0.178	-0.018	11.98
30	5.07	0.787	-0.079	23.82
40	4.75	0.318	-0.032	28.60
50	4.39	0.360	-0.036	34.02
60	4.14	0.250	-0.025	37.78
70	5.06	-0.922	0.092	23.91
80	3.75	1.312	-0.131	43.64
90	3.49	0.254	-0.025	47.46
100	3.74	-0.251	0.025	43.69
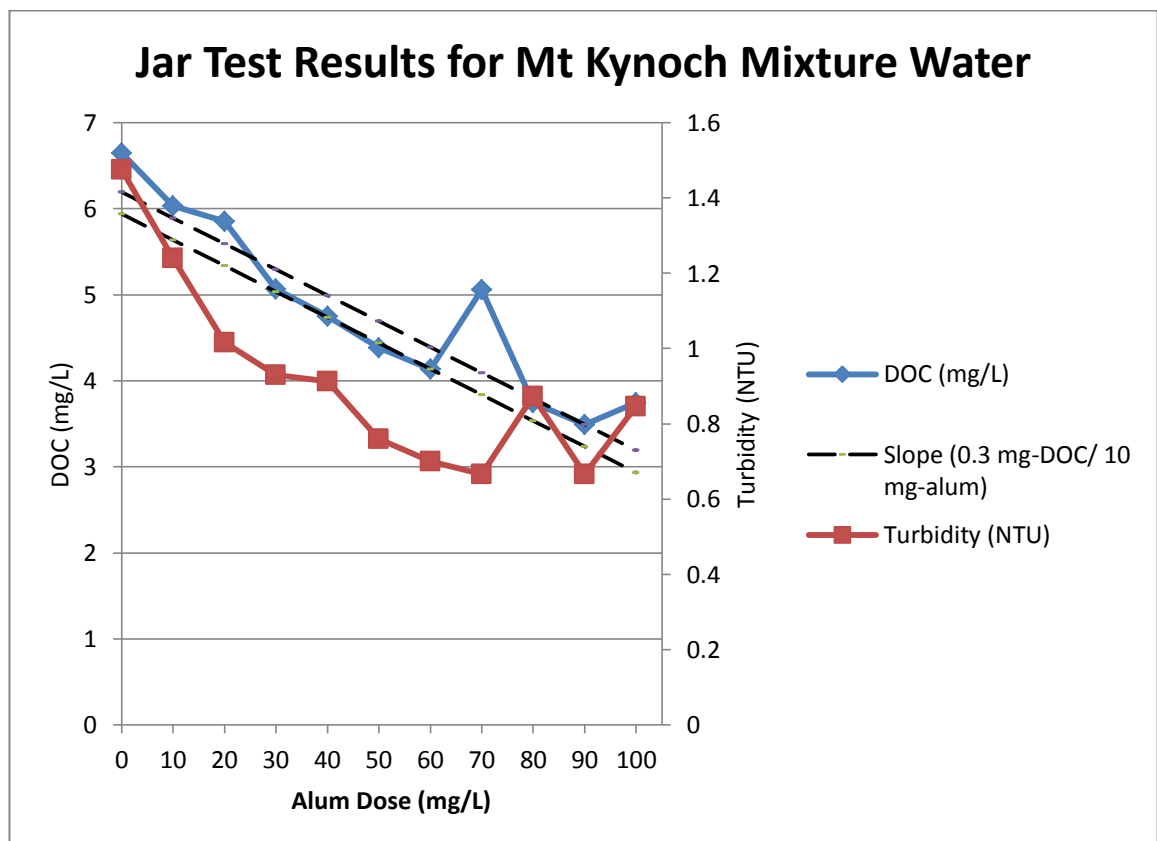
Figure 5-4   Point-to-point curve for determining the PODR for the Mt Kynoch raw water mixture

5.3.3. Continuous Curve Method of Data Analysis

The second method is the continuous curve method which uses regression techniques to draw a best-fit continuous curve through the data points (Agency 1999). To obtain the continuous curve, the experimentally observed residual DOC levels versus the alum dose data was fitted with an exponential decay model of the form:

$$y = a*e^{-b(x)} + C_0 \qquad\qquad (5\text{-}2)$$

where: y = residual DOC in mg/L
       x = coagulant dose in mg/L
      a, b, and C_0 are fitting parameters, found using regression techniques.

The C_0 fitting parameter is significant as it represents the asymptote of the equation and therefore provides an estimate of the refractory organic carbon (the amount that cannot be easily removed by coagulation).

Once this equation is fitted to the data points for each of the water sources, the resultant equation with the fitted parameters is to be derived to determine the slope of the equation at any point. The point of interest, the PODR, occurs when the slope equals to -0.03 (0.3 mg/L DOC removal per 10mg/L of alum). By substituting this slope value into the derived equation, the coagulant dose at the PODR can be determined, and subsequently the organic carbon removal percentage achieved at this point.

The exponential decay model was fitted to the data points from the jar testing of the water from the Japanese Gardens to determine the fitting parameters using the Matlab software (as were the data points from the other water sources). The equation found to represent the observed DOC levels versus the alum dose data for the Japanese Gardens water source was:

$$y = 1.9634 * e^{-0.02(x)} + 1.9271 \qquad\qquad (5\text{-}3)$$

This indicates approximately 1.93 mg/L of organic carbon will not be removed by coagulation and will remain in the water. A plot of this equation is given in Figure 5-5 which shows the measured data points and the predicted points from the equation. The coefficient of determination shows a very close fit between the equation and measured data points.

The first derivative of this equation is of the form $y' = a*(-b)*e^{-b(x)}$, and so for the Japanese Gardens data was found to be:

$$y' = 1.9634*(-0.02)*e^{-0.02(x)} \qquad\qquad (5\text{-}4)$$

To determine the PODR, the y' value was equated to -0.03 and the value of x was determined to find the coagulant dose which results in the achievement of the PODR. This was attained by using the equation of the form:

$$-0.03 = 1.9634*(-0.02)*e^{-0.02(x)} \qquad\qquad (5\text{-}5)$$

By solving this equation for x, the coagulant dose was determined to be 13.46 mg/L. This coagulant dose was then used to identify the DOC level at which the PODR occurred by substituting it back into the original equation fitted to the data. Solving for y when x equalled 13.46, gives a DOC level of 3.43 mg/L. Since the raw water DOC is 3.823 mg/L, this corresponds to a DOC removal of 10.36 percent. The continuous curve method of analysis indicates a coagulant dose of 13.46 mg/L which will achieve DOC reduction of 10.36 percent is the PODR for the water sourced from the Japanese Gardens.
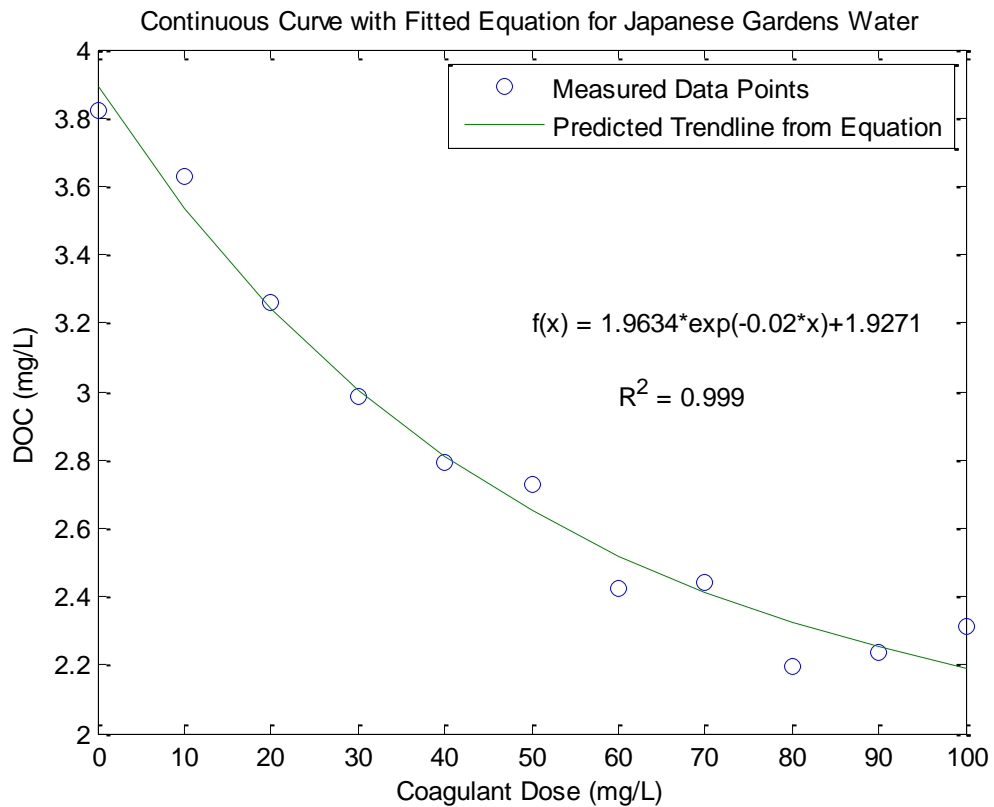
Figure 5-5   **Continuous curve fitted to the Japanese Gardens jar testing data**

The equation found using regression techniques to represent the observed DOC levels versus the alum dose data for the water sourced from Cooby Dam was:

$$y = 3.0994 * e^{-0.0124(x)} + 3.3996 \qquad (5\text{-}6)$$

This equation indicates a higher refractory DOC, indicating it is more difficult to remove organic carbon from this water source and a higher percentage will remain in the water after coagulation. A plot of this fitted equation is given in Figure 5-6. The coefficient of determination is shown again to demonstrate the close fit between the equation and experimentally observed data points.

The first derivative of this equation was found to be:

$$y' = 3.0994*(-0.0124)*e^{-0.0124(x)} \qquad (5\text{-}7)$$

The slope was then again substituted into this equation as -0.03 to find the coagulant dose added at the PODR. This was achieved by using the equation of the form:

$$-0.03 = 3.0994*(-0.0124)*e^{-0.0124(x)} \qquad (5\text{-}8)$$

By solving this equation for x, the coagulant dose was determined to be 19.98 mg/L. The corresponding DOC level for this coagulant dose was calculated to be 5.82 mg/L. As the raw water DOC for Cooby Dam is 6.29 mg/L, this achieves a DOC removal of 7.45 percent. According to the continuous curve method of analysis the PODR occurs when 19.98 mg/L of alum is added to the water which removes 7.45 percent of the DOC.
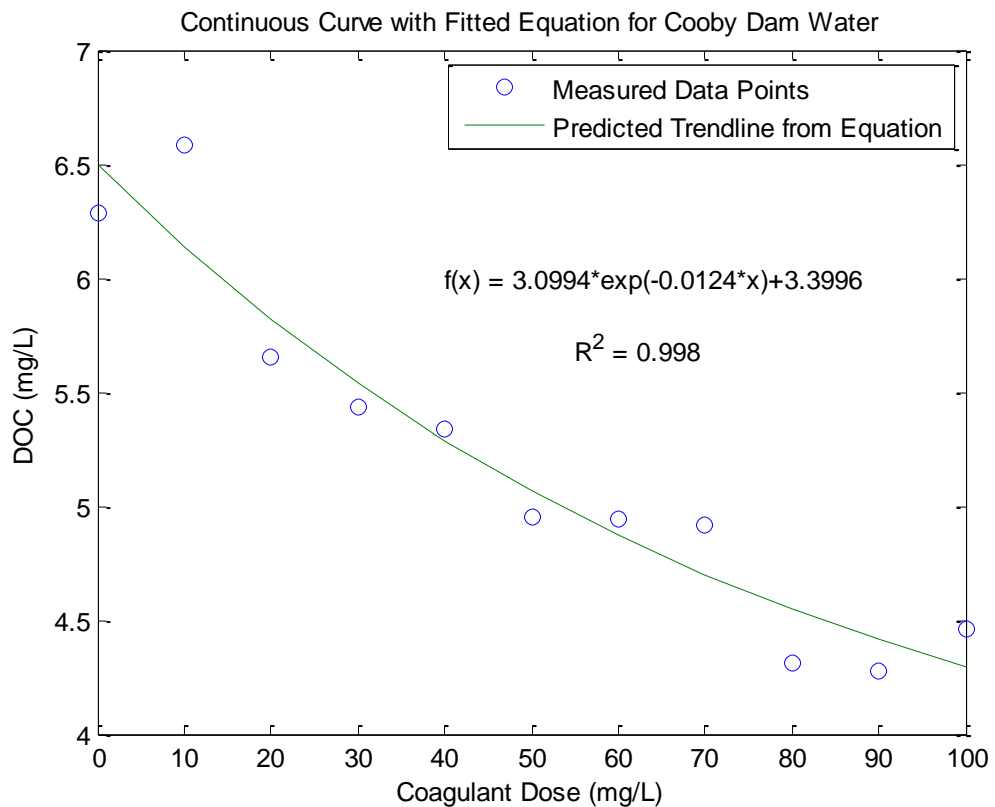
Figure 5-6   Continuous curve fitted to the Cooby Dam jar testing data

For the water sourced from the Perseverance and Cressbrook Dams, the equation fitted to the jar testing data was:

$$y = 4.9761 * e^{-0.0088(x)} + 1.2246 \qquad (5\text{-}9)$$

The refractory DOC amount is given as 1.2246 mg/L, which indicates this much organic carbon will remain in the water even after coagulation. It will not be able to be removed. A plot of the fitted equation can be seen in Figure 5-7, which shows the experimentally observed data points, the predicted points by the equation and the coefficient of determination.

The equation was derived, and the resultant equation was found to be:

$$y' = 4.9761*(-0.0088)*e^{-0.0088(x)} \qquad (5\text{-}10)$$

By substituting in the slope of -0.03, the equation became:

$$-0.03 = 4.9761*(-0.0088)*e^{-0.0088(x)} \qquad (5\text{-}11)$$

The PODR was then determined by solving for the x value. This was found to be a coagulant dose of 42.98 mg/L. Substituting this coagulant dose back into Equation 5-9, a corresponding DOC amount was calculated as 4.63 mg/L. The raw water DOC was 5.86 mg/L and so this gives a removal of 20.96 percent. The point determined as the PODR is the point when a coagulant dose of 42.98 mg/L is added and 20.96 percent of the organic carbon is removed.
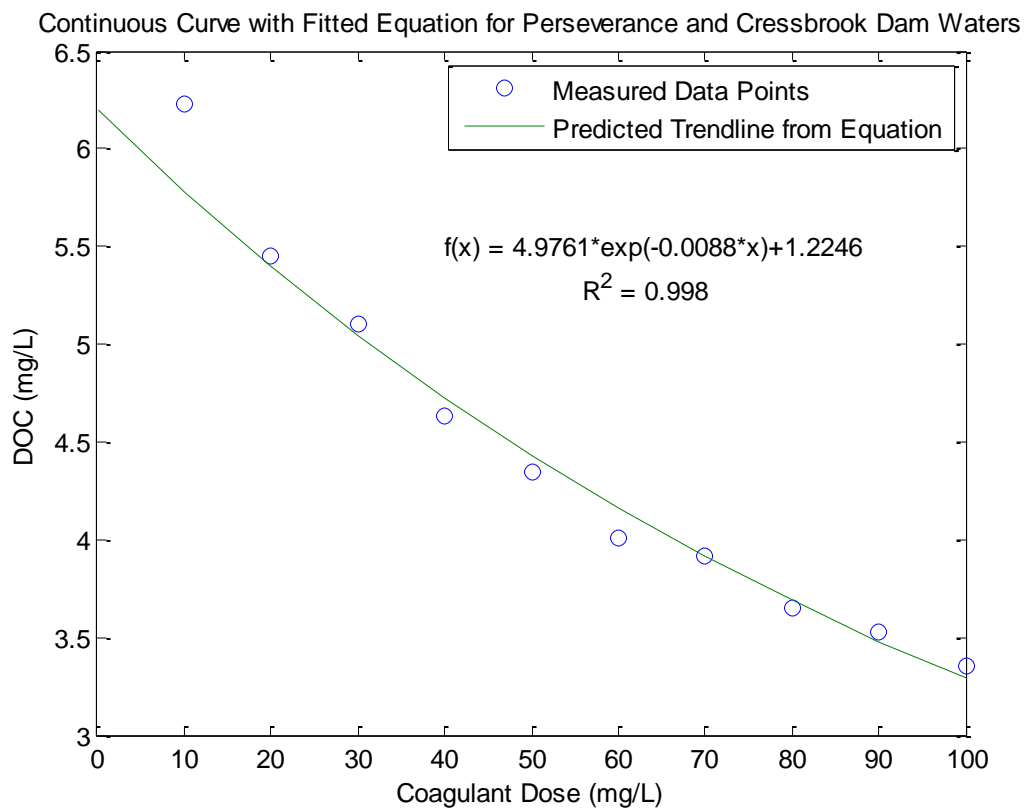
Figure 5-7 **Continuous curve fitted to the Perseverance and Cressbrook Dam jar testing data**

For the last water source of the Mt Kynoch raw water, the fitting parameters were obtained and the equation found to represent the observed DOC levels versus the alum dose data was:

$$y = 3.6471 * e^{-0.0167(x)} + 2.9991 \qquad (5\text{-}12)$$

The refractory DOC amount given by this equation for this water source is approximately 3 mg/L which is not able to be removed by coagulation. This is not quite as high as the refractory DOC of Cooby Dam, but more than that of both the Japanese Gardens, and the Perseverance and Cressbrook Dams. The plot of this equation is given in Figure 5-8. As was the case for all water sources, the coefficient of determination has a value very close to that of one which indicates a well-fitted equation to the measured data points.

The first derivative of the equation fitted to the Mt Kynoch raw water data was found to be:

$$y' = 3.6471*(-0.0167)*e^{-0.0167(x)} \qquad (5\text{-}13)$$

To then find the coagulant dose attributed to the PODR, the value of x was found when the slope was equal to the -0.03 value using the equation:

$$-0.03 = 3.6471*(-0.0167)*e^{-0.0167(x)} \qquad (5\text{-}14)$$

By solving this equation for x, the coagulant dose was determined to be 42.40 mg/L. This coagulant dose was then used to identify the DOC level at which the PODR occurred by substituting it back into the original equation fitted to the data. Solving for y when x equalled 42.4, gives a DOC level of 4.80 mg/L. Since the raw water DOC for this water source is 6.65 mg/L, this corresponds to a DOC removal of 27.87 percent.

The continuous curve method of analysis indicates a coagulant dose of 42.40 mg/L which will achieve DOC reduction of 27.87 percent is the PODR for the Mt Kynoch raw water mixture.
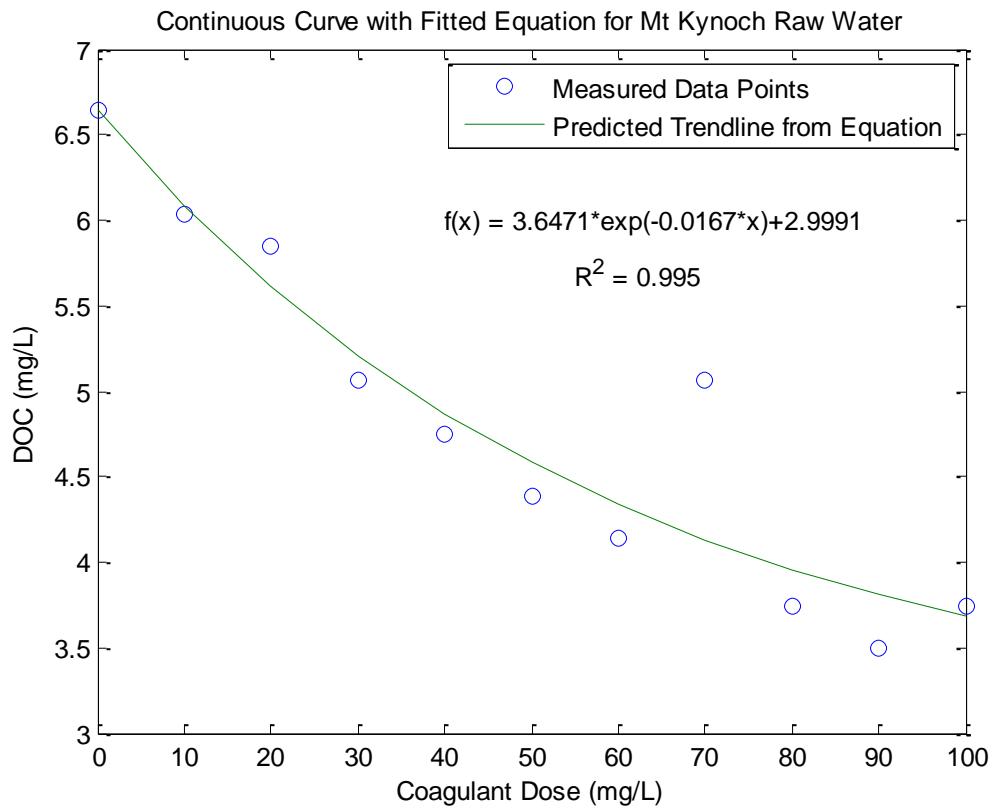
Figure 5-8   Continuous curve fitted to the Mt Kynoch raw water jar testing data

5.3.4. Selection of an Optimum Coagulant Dose for Organic Carbon Removal

The jar tests performed for the purpose of this project are used in the United States to set an alternative TOC removal percentage as per the Step 2 requirement of the DBPR. These values are used to select an optimum coagulant dose for the removal of organic carbon for each of the Toowoomba water sources tested. Two sets of values were obtained from two different methods of analysis.

The continuous curve method of analysis resulted in coagulant doses that produced TOC removal percentages that were considered too low to be suitable. These low coagulant doses were calculated due to the method utilising the value of the rate of DOC removal (or slope of the plot), which is very high as alum is first added but does not necessarily correspond to a high TOC removal percentage. At these doses, a significant proportion of the organic carbon had not been removed and still remained in the waters at these points. With the addition of further alum, a more significant proportion of the DOC is able to be removed. The results from this method therefore, do not have an impact on the selection of an optimum coagulant dose for organic carbon removal.

The point-to-point curve method of analysis produced more logical choices of coagulant doses that gave significantly higher DOC removal percentages. Therefore, these values guide the selection of the optimum coagulant dose for the removal of organic carbon alone.

The optimum coagulant dose (of alum) selected for the removal of organic carbon is: 70 mg/L for both the Japanese Gardens water and water from Perseverance and Cressbrook dams; 90 mg/L for the water sourced from Cooby Dam; and 60 mg/L for the Mt Kynoch raw water mixture.

Despite not contributing to the selection of the optimum coagulant doses, the continuous curve method of analysis still enabled equations to be developed to accurately describe the experimental relationship between the alum dose and residual DOC. Substituting the selected alum dosages back into these developed equations can give a theoretical residual DOC concentration and a removal percentage can then be calculated. Substituting the 70 mg/L into the equation to describe the Japanese Gardens water source, a value of 2.411 mg/L is obtained as the residual DOC concentration and a DOC removal percentage from this value and the raw water DOC concentration of 3.823 mg/L is calculated as 36.9 percent. By following a similar process, the DOC removal percentage for the Cooby Dam water source was calculated to be 29.8 percent. The equation for the Perseverance and Cressbrook Dams resulted in a DOC removal percentage of 33.3 percent and a DOC removal percentage for the Mt Kynoch raw water mixture was calculated to be 34.8 percent. The predicted residual organic carbon concentrations for Cooby Dam, Perseverance and Cressbrook Dams and the Mt Kynoch raw water mixture are 4.42 mg/L, 3.91 mg/L and 4.34 mg/L respectively. The use of the selected optimum coagulant dosages in the developed equations result in more reasonable, and desirable, DOC removal percentages than the coagulant dosages previously used in analysis for this method.

5.4. Turbidity Removal

The turbidity measurements also have to be taken into consideration when selecting an overall optimum coagulant dose. It is impractical to select a coagulant dose which maximises the removal of organic matter if it does not remove the required amount of turbidity. For application in practice in water treatment plants, an optimum coagulant dose is selected for the removal of both turbidity and organic carbon. The turbidity measurements for each of the source waters can be seen in Table 5-10 and graphically in Figures 5-1 to 5-4.

Table 5-10   **Turbidity measurements for each of the source waters after settling**

Alum Dose (mg/L)	Turbidity (NTU)			
	Japanese Gardens	Mt Kynoch Mixture	Perseverance and Cressbrook Dams	Cooby Dam
0	15.0	1.48	1.87	4.50
10	12.4	1.24	1.77	1.65
20	9.94	1.02	1.55	1.45
30	7.91	0.93	1.15	1.25
40	6.25	0.91	0.91	1.14
50	3.88	0.76	0.89	1.06
60	3.15	0.70	0.82	0.97
70	1.02	0.67	0.76	0.97
80	0.80	0.87	0.87	1.15
90	0.95	0.67	0.94	0.81
100	0.78	0.85	0.90	1.13

The turbidity measured in the water sourced from the Japanese Gardens is seen to continually drop with the addition of alum to a final value of 0.78 NTU. Therefore, the maximum removal of turbidity occurs when the 100mg/L dose of alum is added. However, it can also be observed that the removal of turbidity plateaus after the addition of 70mg/L of alum. This indicates that the turbidity removal is reduced for further addition of the coagulant and it does not make as much of a difference to the turbidity levels when more coagulant is added. It is practical to select 70mg/L as a reasonable, optimum dosage of coagulant to achieve a turbidity measurement of 1.02 NTU.

The optimum coagulant dose is selected to be 70mg/L for the removal of turbidity from the raw water mixture from Mt Kynoch water treatment plant. The doses of 70mg/L and 90mg/L achieved the maximum turbidity removal, with both measuring a turbidity of 0.67 NTU. If the same turbidity removal can be achieved by two doses of coagulant, it is more reasonable to select the lower dosage as the optimum.

Similarly, the maximum removal of turbidity also occurs when 70mg/L of alum is added to the water from Perseverance and Cressbrook dams, achieving a turbidity measurement of 0.763 NTU. This is selected as the optimum coagulant dose because maximum removal is achieved and the amount by which turbidity is removed for each incremental increase in coagulant added is considered to be justifiably adequate leading up to this point.

The jar testing of the water sourced from Cooby Dam achieved maximum removal of turbidity with a dose of 90mg/L of alum. This gave a measurement of 0.81 NTU for turbidity. However, the results for the 80mg/L and 100mg/L doses do not follow the observed trend. This may be the result of further addition of alum without pH adjustment, with no clear trend of a decrease in turbidity occurring with increasing alum addition. Therefore, the 70mg/L alum dose could be selected as the optimum coagulant dose achieving a turbidity measurement of 0.97 NTU.

The Australian Drinking Water Guideline for turbidity is 5 NTU (Council & Council 2011), and so each of the selected optimum alum doses achieve compliance with this guideline and are appropriate in this regard.

It is important to note, the removal of turbidity, and organic carbon, is attributed to the coagulation, flocculation and settling which occurs in the jar tests. In practice in water treatment plants, further removal of turbidity and organic carbon will occur due to additional processes such as filtration.

5.5. Selection of Overall Optimum Coagulant Dose

The selection of an overall optimum dose of alum as a coagulant is based upon the doses selected for the removal of both organic carbon and turbidity. This was selected for each of the water sources investigated to account for not only the removal of the organic carbon, which was the primary purpose of the jar testing, but also for the turbidity for the application in water treatment.

For both the Japanese Gardens, and Perseverance and Cressbrook water sources the optimum coagulant dose selected for the removal of organic carbon synchronized with that selected for the removal of turbidity. Therefore, it was a clear selection of a 70 mg/L dose of alum as the overall optimum coagulant dose for both the water sourced from the Japanese Gardens and the Perseverance and Cressbrook Dams.

The optimum coagulant dose for the removal of organic carbon was selected as 90 mg/L for the Cooby Dam water source. A lower dose of 70 mg/L was selected for the removal of turbidity. The overall optimum coagulant dose is selected as the 90 mg/L dose. This corresponds to the optimum removal of organic carbon, in addition to the maximum removal of turbidity. The 70 mg/L dose was previously selected as the optimum dose for turbidity removal as opposed to the 90 mg/L dose, which achieves maximum removal, only due to the uncertainty associated with the turbidity results from the 80 mg/L and 100 mg/L doses. Due to being the selected optimum dose for organic carbon removal and achieving maximum removal of turbidity, the 90 mg/L dose of alum is justifiably selected as the overall optimum coagulant dose for the Cooby Dam water source.

For the raw water mixture from the Mt Kynoch water treatment plant, the alum dose of 60 mg/L was selected as the optimum dose for the removal of the organic carbon.

However, the slightly higher dose of 70 mg/L was selected as the optimum dose for turbidity removal. The 60 mg/L alum dose is selected as the overall optimum dose. This corresponds to the dose selected for the optimum removal of organic carbon, which is given primary significance for the purpose of the project. In terms of turbidity, only a very small percentage of turbidity is further removed by the 70 mg/L dose of alum opposed to the 60 mg/L dose. It is therefore considered satisfactory to accept the turbidity removal which occurred as a result of the addition of the 60 mg/L dose of alum. The overall optimum coagulant dose is selected as the 60 mg/L dose of alum for the raw water mixture from the Mt Kynoch water treatment plant.

5.6. Chapter Summary

The focus of this chapter was the investigation of the removal of organic carbon from the water sources by enhanced coagulation. The results from the jar tests were presented and discussed. The pH measurements were discussed in terms of the target pH values given in the literature as utilised in the United States. Analysis of the removal of the organic carbon was completed by two different methods. Equations were developed, as per the second method of analysis utilised, to predict the residual organic carbon from the coagulant dose. The removal of turbidity was also analysed. Optimum coagulant dosages were selected for turbidity and organic carbon removal.

Chapter 6 Trihalomethane Formation Potential Testing Results and Analysis

This chapter discusses the results from the replication of the jar tests performed with the selected optimum alum dosages and the measurements of the Trihalomethane Formation Potential (THMFP) of both the untreated and treated samples of each water source.

6.1. Validation Jar Tests

The jar tests performed with the optimum alum dosages were replicated to verify the results initially obtained for each of the water sources. The jar testing procedure was followed for one water sample from each of the water sources, dosed with the amount of alum selected as the optimum coagulant dosage. The Japanese Gardens and Perseverance and Cressbrook Dams water samples were treated with 70 mg/L of alum; the Cooby Dam water sample with 90 mg/L and the Mt Kynoch raw water mixture with 60 mg/L. The samples settling after the jar test process can be seen in Figure 6-1.

Figure 6-1　　　**Water samples settling after the jar test with the selected optimum coagulant doses. From left: Japanese Gardens, Cooby Dam, Mt Kynoch raw water mixture, Perseverance and Cressbrook Dams**

The turbidity and DOC were measured for the raw and treated water sources. To minimise error and verify the results, four turbidity measurements and three DOC measurements were taken for the raw and treated water samples of each source. The average values calculated from these results can be seen in Table 6-1.

Table 6-1   **Turbidity and DOC results from validation jar tests for raw and treated water**

	Japanese Gardens	Cooby Dam	Perseverance and Cressbrook Dams	Mt Kynoch raw water mixture
Raw water Turbidity (NTU)	4.80	9.58	0.90	1.93
Treated water Turbidity (NTU)	1.23	0.78	0.75	0.78
Turbidity Removal (%)	**74.5**	**91.8**	**16.2**	**59.7**
Raw water DOC (mg/L)	4.12	6.14	6.55	6.71
Treated water DOC (mg/L)	2.37	4.61	4.42	4.87
DOC Removal (%)	**42.5**	**24.9**	**32.5**	**27.4**

The average values indicate appropriate removal of both turbidity and DOC. The turbidity removal percentages are quite high, resulting in acceptably low turbidity values of the treated water. The exception is the 16.2 percent removal of turbidity from the Perseverance and Cressbrook Dams. However, this is due to the very low measurement of the initial turbidity of the raw water. The removal percentages of the DOC concentrations are within the expected range of values observed from the previous jar tests. The application of the selected optimum coagulant doses of alum has resulted in turbidity removal percentages of: 74.5 percent for the Japanese Gardens; 91.8 percent for Cooby Dam; 16.2 percent for the Perseverance and Cressbrook Dams; and 59.7 percent for the Mt Kynoch raw water mixture. The DOC removal percentages that have been achieved are: 42.5 percent for the Japanese Gardens water; 24.9 percent for Cooby Dam; 32.5 percent for the Perseverance and Cressbrook Dams; and 27.4 percent for the Mt Kynoch raw water mixture. These results can be compared to the results from the original jar tests obtained from treating the water samples with the same alum doses, which are seen in Table 6-2.

Table 6-2   Previous results for the same measurements at the same alum dosages

	Japanese Gardens	Cooby Dam	Perseverance and Cressbrook Dams	Mt Kynoch raw water mixture
Raw water Turbidity (NTU)	15.0	4.50	1.88	1.48
Treated water Turbidity (NTU)	1.02	0.81	0.76	0.70
Turbidity Removal (%)	**93.2**	**82.0**	**59.3**	**52.5**
Raw water DOC (mg/L)	3.82	6.29	5.86	6.65
Treated water DOC (mg/L)	2.44	4.28	3.92	4.14
DOC Removal (%)	**36.2**	**32.0**	**33.1**	**37.8**

In order to make a comparison between the two sets of results, the removal percentages must be the values considered but these are heavily affected by the individual turbidity and DOC measurements. For example, treating the water from the Japanese Gardens with the 70 mg/L dose of alum was able to reduce the turbidity measurement by 74.5 percent in the validation jar test. However, a higher percent of removal of 93.2 percent was achieved previously due to the very high initial turbidity of the raw water. Discrepancies such as this will be present due to the water samples being used for each of the water sources being collected on different dates. Acknowledging this, a comparison can still be made between the values. The replicated jar tests did not produce the same results despite treating the water with the same alum doses. The turbidity measurements had mixed results, with half of the removal percentages improving with the second jar test and half of the treated water samples not performing as well as the first jar test. The DOC removal percentages also varied between the two jar tests but the values were not significantly different than what could be expected.

The DOC removal percentages obtained experimentally correspond fairly well to those predicted by the equations developed to describe the relationship between alum added and DOC residual levels. The equations predict a DOC removal percentage of: 36.9 percent for the Japanese Gardens water; 29.8 percent for the Cooby Dam water; 33.3 percent for the Perseverance and Cressbrook Dams; and 34.8 percent for the Mt Kynoch raw water mixture. The experiment results show these theoretical removal percentages can be exceeded in practice. The observed removal percentages which did not achieve the predicted values only did so by a small proportion.

6.2. Trihalomethane Formation Potential Testing

A secondary objective of these jar tests was to measure the Trihalomethane Formation Potential (THMFP) of both the untreated and treated samples of each water source. THMFP 'is a useful technique to compare the potential of water to form DBPs' (CRC n.d.). These measurements will supplement the measurements of DOC concentrations as DBP pre-cursors in determining the likelihood of the formation of DBPs in the water sources. For investigative purposes, the UV absorption SUVA values were also measured and determined for the water samples during the THMFP testing process. The DOC concentrations were also measured, as discussed in the previous Section 6.1. The results from these measurements for the raw, untreated water can be seen in Table 6-3.

Table 6-3   **Results for the raw water samples for the purpose of measuring the THMFP**

Raw Water	Japanese Gardens	Cooby Dam	Perseverance and Cressbrook Dams	Mt Kynoch raw water mixture
Chlorine Dose (mg/L)	0.26	0.34	0.41	0.39
DOC (mg/L)	4.12	6.14	6.55	6.71
THMFP (ppb)	**132**	**209**	**250**	**231**
UV_{254} (cm^{-1})	0.14	0.11	0.19	0.09
SUVA (L/mg-m)	3.46	1.82	2.95	1.34

The chlorine doses are the doses calculated as the required doses for each particular water sample. The measurements of particular interest are the THMFP results which indicate the tendency for the organic carbon to form DBPs when exposed to the chlorine. The THMFP as parts per billion (ppb) as chloroform ($CHCl_3$) for the raw water samples, in ascending order, are: 132 ppb for the Japanese Gardens; 209 ppb for Cooby Dam; 231 ppb for the Mt Kynoch raw water mixture; and 250 ppb for the Perseverance and Cressbrook Dams. This indicates there is a higher tendency for DBPs to form in the raw water sourced from the Perseverance and Cressbrook Dams than the other untreated water sources. The water sourced from the Japanese Gardens measures the lowest THMFP and is the only water sample which does not contribute to the supply of Toowoomba's drinking water treated by the Mt Kynoch Water Treatment Plant (and therefore exposed to chlorine in practice).

The effect of treating the water samples with the selected optimum coagulant dosages can be seen by the measured results of the treated water, shown in Table 6-4.

Table 6-4   **Results for the treated water samples for the purpose of measuring the THMFP**

Treated Water	Japanese Gardens	Cooby Dam	Perseverance and Cressbrook Dams	Mt Kynoch raw water mixture
Chlorine Dose (mg/L)	0.08	0.21	0.26	0.14
DOC (mg/L)	2.37	4.61	4.42	4.87
THMFP (ppb)	**22.0**	**91.0**	**146**	**82.0**
UV$_{254}$ (cm^{-1})	0.12	0.12	0.06	0.08
SUVA (L/mg-m)	5.15	2.56	1.45	1.59

Treating the water samples reduced the required chlorine dose, DOC concentration and THMFP of each water source. Less chlorine was required to be added to the samples for the purpose of the THMFP testing. The THMFP was reduced from 132 to 22 ppb for the Japanese Gardens water; reduced from 209 to 91 ppb for the water sourced from Cooby Dam; reduced from 250 to 146 ppb for the Perseverance and Cressbrook Dams water; and reduced from 231 to 82 ppb for the Mt Kynoch raw water mixture. Treating the water samples with the selected optimum coagulant dosages has reduced the THMFP by: 83.3 percent for the Japanese Gardens water; 56.5 percent for Cooby Dam; 41.6 percent for Perseverance and Cressbrook Dams; and 64.5 percent for the Mt Kynoch raw water mixture. This demonstrates that enhanced coagulation with the selected optimum coagulant dosages has the ability to significantly decrease the THMFP of each of these water sources, and consequently reduce the potential for the formation of DBPs.

It is expected that the THMFP corresponds with the measured DOC concentration and chlorine dose. For example, the water source with the greatest THMFP will also have the greatest DOC concentration and/or the greatest chlorine dose added to it. For both the raw and treated water samples, the Perseverance and Cressbrook Dam water source has measured the greatest THMFP. This water source did not have the greatest DOC concentration but had the most chlorine added to it for the purpose of the THMFP testing. This greater chlorine dose could be the contributing factor to the high THMFP.

The THMFP is affected by the reactivity of the DOC present in the water. If a water source measures the greatest DOC concentration but not the greatest THMFP, the DOC may not be as reactive as that in a water source with a lower DOC concentration but a greater THMFP. This scenario is reflected by the results obtained for the investigated water sources. The Mt Kynoch raw water mixture measured the greatest DOC concentration before and after treatment with alum, but did not have the greatest THMFP. This may indicate the DOC present in this water source is not as reactive as the DOC present in the Perseverance and Cressbrook Dams water which had a lower concentration but produced a higher THMFP.

THM formation is very complex due to individual factor effects and significant interactions among the factors. This makes it difficult to draw definitive conclusions. The underlying fact is that in order to reduce the concentration of THMs in drinking water, DOC concentrations must be reduced in the water prior to the exposure to chlorine through disinfection (Platikanov et al. 2010).

6.3. Chapter Summary

This chapter discusses the results from the jar tests performed with the selected optimum coagulant dosages. Comparison is made to the previous jar tests performed with the same doses of alum. The results from the trihalomethane formation potential testing were also presented and discussed in this chapter.

Chapter 7 Conclusions

This chapter presents the conclusions of the study and the recommendations for further work.

7.1. Conclusions

A need to monitor the organic matter in Toowoomba water sources has been identified by this research. This has been investigated through the collection of water samples from four Toowoomba water sources, the measurements of NOM-related water characteristics, the analysis of organic carbon removal by enhanced coagulation and the determination of the trihalomethane formation potentials of each water source.

Analytical measurements have enabled the water characteristics of the four water sources to be identified. Cooby Dam was identified as the water source with the greatest average alkalinity of 114 mg $CaCO_3$ /L and dissolved organic carbon concentration of 7.3 mg/L. The remaining water sources measured average dissolved organic carbon concentrations of 4.5 mg/L, 5.7 mg/L and 5.3 mg/L. These values exceed the 2.0 mg/L concentration used in the United States as the trigger for the implementation of enhanced coagulation, concluding further treatment is necessary for these Toowoomba water sources. The calculated SUVA values indicate this organic matter is primarily made up of non-humic substances. It was observed the measured water characteristics do not demonstrate a clear, consistent correlation with the rainfall data.

Upon comparison of the water characteristics of the Toowoomba water sources with those measured for other water sources in previous studies, the differences were too great to be able to draw similar conclusions for the water sources from earlier studies.

Experimental jar testing results have proven enhanced coagulation to be an effective treatment technique for the targeted removal of organic carbon from each of the water sources. Increased coagulant doses of alum significantly reduced the turbidity and dissolved organic carbon concentration of each water source. Optimum coagulant dosages were selected upon analysis of the results as 70 mg/L for both the Japanese Gardens and Perseverance and Cressbrook Dams, 90 mg/L for the Cooby Dam water source, and 60 mg/L for the Mt Kynoch raw water mixture. These coagulant dosages reduced the dissolved organic carbon concentrations by 36.2 percent, 33.1 percent, 32.0 percent, and 37.8 percent respectively.

Equations were developed using regression techniques for each water source to theoretically predict the residual organic carbon concentration from the coagulant dose. These equations predict the residual organic carbon concentrations for when the water sources are treated with the selected optimum coagulant doses as 2.41 mg/L, 4.42 mg/L, 3.91 mg/L and 4.34 mg/L for the Japanese Gardens, Cooby Dam, Perseverance and Cressbrook Dams, Mt Kynoch raw water mixture water sources respectively. The equations also indicate the refractory amount of organic carbon that is not easily

removed by coagulation at all which are 1.93 mg/L for the Japanese Gardens, 3.40 mg/L for Cooby Dam, 1.22 mg/L for Perseverance and Cressbrook Dams, and 3.00 mg/L for the Mt Kynoch raw water mixture.

The trihalomethane formation potential results were also significantly reduced by treating the water sources with the selected optimum coagulant dosages as reflected by the measurements taken of the untreated and treated water samples. The measurements were reduced from 132 to 22 ppb for the Japanese Gardens water; reduced from 209 to 91 ppb for the water sourced from Cooby Dam; reduced from 250 to 146 ppb for the Perseverance and Cressbrook Dams water; and reduced from 231 to 82 ppb for the Mt Kynoch raw water mixture.

This research has enabled conclusions to be drawn regarding the amount of organic matter within Toowoomba water sources, the removal of this by enhanced coagulation, and the trihalomethane formation potential of these water sources. It is highly recommended these conclusions are further investigated in future work.

7.2. Recommendations for Further Work

The scope of this project is somewhat narrow and so other aspects of this topic have been identified as having the potential to be investigated in further work. Recommendations for further work include:

- Investigate the seasonal effect of NOM concentrations by sampling year-round;
- Aim to identify the specific causes and nature of the NOM present in the water sources;
- Consider the use and effect of different coagulants; and
- Study the treated water from Mt Kynoch water treatment plant to give an indication of the effectiveness of the current water treatment for the removal of organic matter.

A more in-depth investigation is recommended for the water sources of Toowoomba to conclusively determine if further treatment is necessary and feasible, and how this would best be applied in practice.

7.3. Chapter Summary

This chapter concluded the results of this dissertation and presented recommendations for further work. It was found the dissolved organic carbon concentrations of the water sources exceeded the limit for which is considered suitable for conventional treatment in the United States, and so further treatment is recommended for Toowoomba water sources. Enhanced coagulation was proven to significantly reduce the concentrations of organic carbon in the water sources. A number of recommendations were suggested for further work including investigating the seasonal effect of NOM, the use of different coagulants and identifying the specific causes of the organic matter.

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Appendix A – Project Specification

University of Southern Queensland

FACULTY OF HEALTH, ENGINEERING AND SCIENCES

ENG4111/4112 Research Project

PROJECT SPECIFICATION

FOR: **JAMIE MCINTYRE**

TOPIC: MONITORING AND REMOVAL OF NATURAL ORGANIC MATTER (NOM) FROM TOOWOOMBA WATER SOURCES

SUPERVISOR: Dr. Vasanthadevi Aravinthan

ENROLMENT: ENG4111 – S1, On campus, 2015
ENG4112 – S2, On campus, 2015

PROJECT AIM: This project aims to monitor the amount of natural organic matter in the water sources of Toowoomba and investigate the removal of this by enhanced coagulation.

PROGRAMME: **Issue A, 12 March 2015**

1. Conduct an extensive literature review on the current research undertaken on NOM and resultant trihalomethane (THM) formation potential in countries such as the United States and in Australia to identify the research gaps.
2. Monitor NOM by taking water samples from different Toowoomba water sources such as Cooby Dam, raw water from Mt. Kynoch Water Treatment Plant, Perseverance Dam and the Japanese Gardens on a weekly basis and by measuring pH, conductivity, alkalinity, turbidity, dissolved organic content (DOC), and UV absorption.
3. Analyse the data obtained in Step 2 and explain the tendency by correlating the NOM data with the rainfall information obtained from Bureau of Meteorology.
4. Perform enhanced coagulation to determine the dosage required for maximum NOM removal for each of the water sources by following the procedure described by the US EPA using alum as the coagulant.
5. Critically analyse the results obtained in Step 4 and evaluate the performance of the coagulants in removing NOM of different nature.
6. Investigate the trihalomethane (THM) formation potential of raw and treated water using the optimum coagulant dosage.
7. Submit an academic dissertation on the research.
8. As time permits:
Conduct similar coagulations as described in Step 4 using the statistical technique of Design of Experiments (DoE) and find out the optimum dosage required to achieve maximum NOM removal employing surface response methodology using Minitab software.

Appendix B – Risk Assessment

Risk Assessment

It is a necessary requirement of this project to conduct an assessment of the risks associated with the project testing. The risks must be identified, the likelihood and consequence of which are to be evaluated, and all control measures are to be identified to form an appropriate risk management plan.

Risk Identification

The risks associated with the project testing, before and after control measures are followed, can be identified as:

Risks without Control	Risks with Control
Risk of a traffic accident while driving to collect water samples can have devastating consequences such as serious injury or even death.	With control measures in place, the risk is unlikely to happen.
Safety risks such as slips or emergencies are involved with the collecting of water samples onsite at Mt Kynoch	The risk is small and unlikely to happen.
Risk of injury from slipping can be caused by the spilling of water in the laboratory.	The risk is unlikely to happen and the consequences will be minor.
Working with glassware poses a likely risk of minor injuries and/or cuts if breakages should occur.	The likelihood of breakages occurring is reduced by using appropriate caution and so the risk is minimised.
Working with acid poses serious health risks of toxicity if inhaled, burns or serious damage to eyes or skin if contact occurs.	The risk is reduced to a minor risk if appropriate PPE is worn.
Risk of electrocution from working with water and electrical equipment is a serious risk with serious consequences, ultimately death.	With control measures in place, the risk of electrocution is minor.

There are minimal risks associated with the sustainability of this project. The risks pertaining to the environment are kept at a minimum by using a non-intrusive method to collect water samples and proper disposal of waste, chemicals and any hazardous materials. There are no hazards which future users of this project will be at risk of.

Risk Control

A number of precautionary measures are implemented, and adhered to, to ensure proper risk management practices. These include:

- A driver's licence is held by the driver of a vehicle,
- Water samples are taken while accompanied to reduce safety risks,
- Water spills are cleaned immediately to reduce the risk of a slip,
- Appropriate caution is taken when handling glassware,
- A safety induction was conducted before commencing work in the laboratory,
- Appropriate Personal Protective Equipment (PPE) is always worn when in the laboratory, including a lab coat, gloves, appropriate enclosed footwear and glasses,
- The MSDS was consulted for each acid used,
- Additional measures were taken when handling acids, such as the use of the fume hood and wearing of face protection,
- An emergency wash station is located in the laboratory for use in the case of contact with acid, and
- Appropriate caution is taken when working with water and electrical equipment.

Risk Evaluation

The likelihood of the identified risks with control measures in place can be categorised as 'unlikely' and the consequence as 'minor'. This results in a risk rating of 'low' for the project testing, and represent a low level of risk to those involved. These risks can therefore be managed by routine procedures. If appropriate caution is not taken where required, a higher level of risk would be associated with this testing.

Appendix C – Analytical Measurements Data

		Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Average
pH	JG	7.69	7.83	7.81	8.68	7.08	8.19	7.41	7.43	7.65	8.01	7.778
	Cooby	8.77	7.82	7.59	7.78	7.74	8.09	7.93	8.00	8.12	7.93	7.977
	Persev.	7.27	7.19	7.08	7.12	7.29	7.34	7.31	7.41	7.34	7.29	7.264
	Mix	-	7.06	7.11	7.05	7.04	7.39	7.29	7.34	7.30	7.26	7.204
Conductivity (μS)	JG	277	336	268	272	268	296	104.4	113.5	133	179.1	224.7
	Cooby	728	742	680	736	757	744	722	725	733	733	730
	Persev.	263	262	262	261	267	262	261	256	257	258	260.9
	Mix	-	263	260	288	267	282	261	280	259	269	269.9
TDS (ppm)	JG	138	169	134	136	133	148	52.1	56.5	66.4	89.5	112.25
	Cooby	364	371	340	369	378	372	361	363	367	367	365.2
	Persev.	131	131	131	131	133	132	131	128	129	129	130.6
	Mix	-	132	130	144	133	141	131	140	129	135	135
Turbidity (NTU)	JG	14.47	15.57	35.67	19.1	24.93	21.4	18.8	12.5	25.4	13.37	20.121
	Cooby	3.12	1.55	2.45	2.51	2.14	3.55	8.39	3.66	1.91	1.75	3.103
	Persev.	1.49	1.58	1.87	1.02	1.27	1.31	2.94	4.42	3.02	2.39	2.131
	Mix	-	1.72	1.75	8.09	9.45	0.98	7.027	5.41	7.56	4.19	5.131
Alkalinity (mg CaCO$_3$ /L)	JG	45	63	46	35	32	38	19	20.5	26.4	31.4	35.63
	Cooby	115	146.67	110	110	112.5	111.75	110	106.75	106.75	108.65	113.8
	Persev.	79	96	73.33	70	75	75	75	68.5	69.9	70.2	75.193
	Mix	-	100	73.33	74	74	73.5	76	72.5	70.3	72.25	76.209
DOC (mg/L)	JG	4.866	3.338	4.069	4.399	5.52	5.715	4.112	4.822	3.668	4.605	4.5114
	Cooby	7.915	6.459	6.502	6.153	6.448	5.972	8.667	6.058	12.74	5.976	7.289
	Persev.	5.862	4.614	5.315	5.121	4.925	4.881	5.315	5.239	11.01	5.208	5.749
	Mix	-	4.568	4.575	4.616	4.762	4.844	5.655	5.036	4.506	8.782	5.260
UV$_{254}$ (cm^{-1})	JG	0.092	0.094	0.097	0.116	0.113	0.096	0.16	0.099	0.102	0.081	0.105
	Cooby	0.111	0.093	0.089	0.112	0.093	0.098	0.146	0.11	0.103	0.104	0.1059
	Persev.	0.092	0.105	0.105	0.115	0.101	0.1	0.132	0.151	0.138	0.123	0.1162
	Mix	-	0.091	0.09	0.111	0.1	0.096	0.128	0.131	0.132	0.114	0.1103

		Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Average
SUVA (L/mg-m)	JG	1.8907	2.816	2.3839	2.6370	2.0471	1.6798	3.8911	2.0531	2.7808	1.7590	2.3938
	Cooby	1.4024	1.4399	1.3688	1.8203	1.4423	1.6410	1.6846	1.8158	0.8085	1.7403	1.5164
	Persev.	1.5694	2.2757	1.9755	2.2457	2.0508	2.0484	2.4835	2.8822	1.2534	2.3618	2.1147
	Mix	-	1.9921	1.9672	2.4047	2.0999	1.9818	2.2635	2.6013	2.9294	1.2981	2.1709
Iron (ppm)	JG	-	-	0.2895	0.3158	0.3567	0.1852	0.2265	0.2382	0.2858	0.1454	0.2554
	Cooby	-	-	0.0779	0.0952	0.0233	0.064	0.0316	0.03	0.0793	0.0475	0.0561
	Persev.	-	-	0.1286	0.1103	0.0029	0.0154	0.05	0.1183	0.0793	0.0951	0.07499
	Mix	-	-	0.0557	0.0648	0.00	0.0176	0.0117	0.045	0.093	0.1131	0.0494

14-Apr

No.	Name	Amount mg/L Fluoride ECD_1	Amount mg/L Chloride ECD_1	Amount mg/L Nitrite ECD_1	Amount mg/L Bromide ECD_1	Amount mg/L Nitrate ECD_1	Amount mg/L Phosphate ECD_1	Amount mg/L Sulphate ECD_1
1	Blank	n.a.	n.a.	n.a.	-767.0744	n.a.	n.a.	n.a.
2	10	9.8822	10.4026	10.0458	10.0000	10.3228	10.2979	10.2857
3	20	20.1570	19.4632	19.9389	20.0000	19.5696	19.6028	19.6191
4	50	49.9607	50.1342	50.0153	n.a.	50.1076	50.0993	50.0952
5	Cooby	-2.5214	168.6236	-1.8138	-346.7839	0.7037	1.0896	5.1683
6	Perseverance	-2.6339	35.9277	n.a.	-270.6865	0.7528	n.a.	1.5765
7	Mixed	-2.6559	42.5328	n.a.	-272.9900	0.7508	n.a.	1.8989
8	J.G.	-2.6415	57.7197	n.a.	-134.2657	0.6987	n.a.	6.7800
9	shutdown	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	69.547	384.804	78.186	-1,761.801	82.906	81.090	95.424
	Average:	9.935	54.972	19.547	-251.686	11.844	20.272	13.632
	Rel.Std.Dev:	198.616 %	96.007 %	113.441 %	-106.559 %	154.941 %	104.933 %	126.286 %

28-Apr

No.	Name	Amount mg/L Fluoride ECD_1	Amount mg/L Chloride ECD_1	Amount mg/L Nitrite ECD_1	Amount mg/L Bromide ECD_1	Amount mg/L Nitrate ECD_1	Amount mg/L Phosphate ECD_1	Amount mg/L Sulphate ECD_1
1	Blank	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	STD 1	10.3644	10.1485	10.3228	9.9217	9.8792	9.8134	9.7334
3	STD 2	19.7407	19.9025	19.7782	20.0515	19.5199	20.1228	20.1734
4	STD 3	50.0328	50.0093	50.0245	49.9951	50.2162	49.9882	49.9838
5	J.G.	0.0276	66.3220	n.a.	4.0089	n.a.	n.a.	n.a.
6	Cooby	0.1875	161.1245	0.1322	7.4031	n.a.	n.a.	0.1319
7	Perseverance	0.0874	37.0601	n.a.	1.3768	0.0759	n.a.	n.a.
8	Mixed	0.0987	42.8474	n.a.	1.7111	0.0773	n.a.	n.a.
9	Q.S. 20ppm	20.5607	20.7449	20.5163	20.2591	20.1410	20.8354	19.7156
10	shutdown	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	101.100	408.159	100.774	114.727	99.910	100.760	99.738
	Average:	12.637	51.020	20.155	14.341	16.652	25.190	19.948
	Rel.Std.Dev:	138.535 %	94.219 %	92.492 %	113.079 %	112.104 %	68.608 %	93.763 %

5-May

No.	Name	Amount mg/L Fluoride ECD_1	Amount mg/L Chloride ECD_1	Amount mg/L Nitrite ECD_1	Amount mg/L Bromide ECD_1	Amount mg/L Nitrate ECD_1	Amount mg/L Phosphate ECD_1	Amount mg/L Sulphate ECD_1
1	Blank	n.a.	n.a.	n.a.	0.2257	n.a.	n.a.	n.a.
2	STD 1	10.4726	10.2186	10.3930	10.1447	10.1677	9.9766	9.9778
3	STD 2	19.6643	19.8567	19.7257	19.9036	19.6315	20.0158	20.0145
4	STD 3	50.0423	50.0136	50.0321	50.0096	50.1139	49.9984	49.9986
5	J.G.	0.0460	22.2296	n.a.	1.8583	n.a.	n.a.	n.a.
6	Cooby	0.1614	156.0331	0.1325	7.4596	0.0253	n.a.	n.a.
7	Perseverance	0.0892	37.0199	n.a.	1.6665	0.0946	n.a.	n.a.
8	Mixed	0.0892	37.2256	n.a.	1.6668	0.0959	n.a.	n.a.
9	Q.S. 10ppm	10.9665	10.6512	10.8436	10.5527	10.6104	10.6030	10.2293
10	shutdown	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	91.531	343.248	91.127	103.488	90.739	90.594	90.220
	Average:	11.441	42.906	18.225	11.499	12.963	22.648	22.555
	Rel.Std.Dev:	150.431 %	111.368 %	104.722 %	137.029 %	138.593 %	83.020 %	83.720 %

12-May

No.	Name	Amount mg/L Fluoride ECD_1	Amount mg/L Chloride ECD_1	Amount mg/L Nitrite ECD_1	Amount mg/L Bromide ECD_1	Amount mg/L Nitrate ECD_1	Amount mg/L Phosphate ECD_1	Amount mg/L Sulphate ECD_1
1	Blank	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	STD 1	10.4654	10.2263	10.4235	9.9503	10.1222	9.9773	9.8659
3	STD 2	19.6701	19.8520	19.7097	20.0327	19.5772	20.0152	20.0876
4	STD 3	50.0412	50.0140	50.0318	49.9969	50.1447	49.9984	49.9918
5	J.G.	n.a.	23.5899	n.a.	2.1087	n.a.	n.a.	n.a.
6	Cooby	0.1560	154.4235	n.a.	7.4853	0.0301	n.a.	n.a.
7	Perseverance	0.0894	36.5754	n.a.	1.6414	0.1081	n.a.	n.a.
8	Mixed	0.0985	43.8297	n.a.	2.1115	0.1024	n.a.	n.a.
9	Q.S. 50 ppm N	n.a.	n.a.	n.a.	n.a.	41.9707	n.a.	n.a.
10	Q.S. 10ppm	10.9924	10.7702	10.9374	10.5037	10.6523	10.6238	10.4004
11	shutdown	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	91.513	349.281	91.102	103.830	132.708	90.615	90.346
	Average:	13.073	43.660	22.776	12.979	16.588	22.654	22.586
	Rel.Std.Dev:	137.013 %	107.877 %	81.947 %	124.591 %	117.818 %	82.980 %	83.521 %

19-May

No.	Name	Amount mg/L Fluoride ECD_1	Amount mg/L Chloride ECD_1	Amount mg/L Nitrite ECD_1	Amount mg/L Bromide ECD_1	Amount mg/L Nitrate ECD_1	Amount mg/L Phosphate ECD_1	Amount mg/L Sulphate ECD_1
1	Blank	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	STD 1	10.4986	10.2440	10.4325	10.0077	10.1205	10.0012	9.9396
3	STD 2	19.6461	19.8404	19.7026	19.9950	19.5277	19.9992	20.0390
4	STD 3	50.0444	50.0151	50.0330	50.0005	50.1648	50.0001	49.9964
5	J.G.	0.0518	26.4048	n.a.	2.2947	n.a.	0.0783	n.a.
6	Cooby	0.1731	156.9238	0.1555	7.7185	n.a.	n.a.	0.1562
7	Perseverance	0.0923	36.7240	n.a.	1.5407	0.1166	n.a.	n.a.
8	Mixed	0.0883	37.1388	n.a.	1.6388	0.1169	n.a.	n.a.
9	Q.S. 50 ppm N	n.a.	n.a.	n.a.	n.a.	42.9295	n.a.	n.a.
10	Q.S. 10ppm	10.9804	10.7106	10.9136	10.5696	10.6042	10.6406	10.5228
11	shutdown	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	91.575	348.002	91.237	103.765	133.580	90.719	90.654
	Average:	11.447	43.500	18.247	12.971	19.083	18.144	18.131
	Rel.Std.Dev:	150.336 %	109.998 %	104.506 %	124.851 %	104.950 %	105.557 %	105.630 %

26-May

No.	Name	Amount mg/L Fluoride ECD_1	Amount mg/L Chloride ECD_1	Amount mg/L Nitrite ECD_1	Amount mg/L Bromide ECD_1	Amount mg/L Nitrate ECD_1	Amount mg/L Phosphate ECD_1	Amount mg/L Sulphate ECD_1
1	Blank	n.a.	0.0779	n.a.	0.0554	n.a.	n.a.	n.a.
2	STD 1	10.2788	10.1398	10.3456	9.8295	10.1803	9.7821	9.7993
3	STD 2	19.7982	19.9070	19.7582	20.1152	20.1735	20.1484	20.1344
4	STD 3	50.0274	50.0093	50.0286	49.9880	49.8945	49.9842	49.9864
5	J.G.	n.a.	38.8943	n.a.	2.8230	n.a.	0.0847	n.a.
6	Cooby	0.1536	169.0597	0.1101	7.5368	0.0159	n.a.	0.1402
7	Perseverance	0.0919	35.9836	n.a.	1.5921	0.1129	n.a.	n.a.
8	Mixed	0.0918	39.3798	n.a.	1.8348	0.1103	n.a.	n.a.
9	Q.S. 50 ppm N	n.a.	n.a.	n.a.	n.a.	41.1852	n.a.	n.a.
10	Q.S. 10ppm	10.4230	10.1569	10.5092	9.9396	10.3201	9.9817	9.8850
11	shutdown	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	90.865	373.608	90.752	103.714	131.993	89.981	89.945
	Average:	12.981	41.512	18.150	11.524	16.499	17.996	17.989
	Rel.Std.Dev:	138.152 %	122.043 %	105.388 %	136.323 %	117.371 %	106.900 %	106.920 %

Titration Results Example for Alkalinity Calculation

26/5 Sample measured on 26/5 with 0.1N HCl

Japanese Gardens	pH	Acid Added (mL)
	7.58	0
	4.3	0.628

Mt Kynoch:

Cooby	pH	Acid Added (mL)
	7.84	0
	4.32	2.173

Mt Kynoch: Perseverance	pH	Acid Added (mL)
	7.35	0
	4.31	1.404

Mixed Mt

Kynoch	pH	Acid Added (mL)
	7.3	0
	4.3	1.445

Alkalinity Calculations

	mg CaCO3 / L	
Japanese Gardens	31.4	to pH 4.3
Mt Kynoch: Cooby	108.65	to pH 4.3
Mt Kynoch: Perseverence	70.2	to pH 4.3
Mixed Mt Kynoch	72.25	to pH 4.3

N	0.1
Sample	100

Appendix D – Additional Jar Test Data for Japanese Gardens

Jar Test 1 Results

Japanese Gardens water without pH adjustment

	Alum Added (ppm)	pH	Turbidity (NTU)	Alkalinity (mg CaCO3/L)	DOC (mg/L)	Incremental DOC Removal (mg/L)	Incremental Slope	DOC Removal (%)	Residual Alum (ppm)
Raw Water	0	8.23	6.4	50.5	7.077	-	-	-	-
	10	7.36	5.953333333	-	3.334	3.743	-0.3743	52.8896425	0.3846
	20	7.01	4.806666667	-	3.089	0.245	-0.0245	56.3515614	0.1231
	30	6.68	4.063333333	-	3.102	-0.013	0.0013	56.16786774	0.1692
	40	6.44	3.4	-	2.971	0.131	-0.0131	58.01893458	0.0769
	50	6.26	2.673333333	-	2.856	0.115	-0.0115	59.64391691	0.1231
	60	6.09	1.103333333	-	2.6	0.256	-0.0256	63.2612689	0.0308
	70	5.94	1.056666667	-	2.563	0.037	-0.0037	63.7840893	0.1231
	80	5.77	0.616666667	-	2.843	-0.28	0.028	59.82761057	0.4154
	90	5.59	0.973333333	-	2.217	0.626	-0.0626	68.6731666	0.0615
	100	5.39	0.82	-	2.664	-0.447	0.0447	62.3569309	0.0000