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Chlorine Decay Modelling to Predict Disinfectant and Disinfectant by-Products (DBPs) Formation in Water Distribution System

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Declaration

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

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

Signature: ….. ….

Date: 11/11/2018

DEDICATIONS

This dissertation is dedicated to my mother, whom I owe my whole life to, to my sisters and my father for their love and support.

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ABSTRACT

Chlorine is one of the most popular disinfectants that have been used within water distribution systems. Chlorine reaction with many compounds in water, however, causes chlorine to decay. Hence its concentration and thus ability for disinfecting declines over time. Since a minimum disinfectant residual is required to be maintained at the customer tap, it is important that chlorine decay within water distribution systems is predicted accurately so that primary and secondary disinfection can be managed effectively.

Several chlorine decay models have been so far proposed by many researchers in order to estimate the chlorine residuals within water distribution systems. Existing chlorine decay models include data-based (empirical) and process-based (theoretical) models.

The following process-based models have been used or referenced more broadly by the researchers and also by various water utility officials:

- First Order Model (FOM)
- Second Order Model (SOM)
- Parallel First Order Model (PFOM)
- Extended Second Order Model (ESOM)
- Parallel Second Order Model (PSOM)

Whilst some water utility operators prefer to use simpler models such as FOM for prediction of chlorine residuals, other water authorities and researchers believe accuracy of chlorine decay models is prominent to achieve acceptable results for chlorine decay within water distributions systems and thus use more sophisticated models such as PFOM, ESOM and PSOM.

All existing chlorine decay models have some advantages and disadvantages over one another. However, there have been many debates and discussions between researchers and scientists about preference of some models over others. Nonetheless, it is important to select a suitable model for prediction of chlorine residuals in water distribution systems. Furthermore, since demand for standardization of chlorine decay modelling approaches is increasing, it is essential to propose main criteria for selection of chlorine decay models to predict chlorine residuals within water distribution networks.

The main aim of this research project is to generally develop understanding of chlorine decay and formation of disinfectant by-products using current popular chlorine decay models. Following the investigation completed by a research project undertaken during previous master of philosophy study, in this project, initially, reliability of different models for different waters with different qualities was investigated, to determine the model parameters and observe how various models fit existing measured data. Main drawbacks of the current popular process-based models were highlighted. Existing models with major weaknesses were modified to produce more reliable predictions. As result, two new chlorine decay models have been proposed and their results compared with other models. The first new model is called the modified parallel first order model (MPFOM) and was compared against the parallel first order model (PFOM). The second new model was developed based on the extended second order model (ESOM) and was referred to as the modified second order model (MSOM). Then main criteria for performance improvement of the models were defined. The nominated chlorine decay models were compared against some of the defined criteria and the best chlorine decay model was endorsed. In the end, chlorine decay and formation of disinfection by-products in one of the water distribution systems in Western Australia was modelled as a case study.

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Glossary

The following symbols are used in this thesis:

DBP = Disinfection By-Products
DPD = Diethyl-p-Phenylene Diamine
DOC = Dissolved Organic Carbon
DON = Dissolved Organic Nitrogen
EDTA = Ethylenedinitrilotetraacetic Acid
FRA = Fast Reacting Agent
HAA = haloacetic acids
NDMA = Nitrosdimethylamine
N-DBP = Nitrgenous Disinfection By-Products
NH_3 = Ammonia
NO_2 = Nitrite
NO_3 = Nitrate
NO_x-N = Total of nitrite and nitrate
NOM = Natural Organic Matter
SRA = Slow Reacting Agent
TOC = Total Organic Carbon
TON = Total Organic Nitrogen
THM = Triahalomethane
TTHM = Total Trihalomethane
TDS = Total Dissolved Solids

1. Introduction

1.1. Background Summary

All distributed drinking water receives some form of disinfection at the end of treatment process. A minimum disinfectant residual should be maintained at the customer tap. The most popular disinfectant is chlorine. Chlorine reacts with compounds in water and hence decays.

As chlorine decays, it loses its potential to effectively achieve the main objectives of disinfection of water in distribution systems (primary and secondary disinfection). In order to overcome this issue more chlorine can be added to water to compensate its decay. However, the amount of chlorine added to the water is very important. If the initial chlorine dosing concentration is too low, there may not be a residual left at the end of the distribution system to protect water against reoccurrence of any potential contamination. If the dosing rate is too high, it can lead to customer complaints, corrosion of the pipe network or formation of by-products, including trihalomethanes (THMs), which are suspected carcinogens. One of the methods for determining the right amount of chlorine that needs to be added to water before it leaves the treatment plant is to perform trials frequently. This method, however, is very time and resource consuming and thus is cost prohibitive. This is because chlorine decay behaviour depends significantly on many variable parameters/factors including water quality characteristics, temperature, hydraulics of distribution system etc. As a result, the most cost effective method to achieve the right chlorination regime is to mathematically model chlorine decay within distribution system. However, before any attempt could be made to understand the decay characteristics in the distribution system, chlorine decay in bulk water has to be correctly described. There have been significant attempts so far to understand the mechanisms of chlorine decay in bulk water and within the water distribution systems. However, due to complexity of chlorine reactions with a variety of organic and inorganic species, it appears that still extensive investigation in this filed needs to be carried out.

Many chlorine decay models including data-based (empirical) and process-based (theoretical) models have been so far proposed by many researchers. Whilst there has been significant improvement in development of chlorine decay models, there is still room for improvement due to complexity of chlorine decay and dependency of its behaviour on many known and unknown parameters. Amongst all proposed chlorine decay models, the following process-based models have been used or referenced more broadly by the researchers and also by various water utility officials:

- First Order Model (FOM)
- Second Order Model (SOM)
- Parallel First Order Model (PFOM)
- Extended Second Order Model (ESOM)
- Parallel Second Order Model (PSOM)

Whilst some water utility operators give preference to simpler models such as FOM for prediction of chlorine residuals over water distributions systems, other water authorities and researchers believe accuracy of chlorine decay models is very important and thus prefer to use more sophisticated models such as PFOM, ESOM and PSOM. Although all above mentioned models have some advantages and disadvantages over one another, there have been many debates and discussions between researchers and scientists about preference of some models over others. Nonetheless, it is important to select a suitable model for prediction of chlorine residuals in water distribution systems. Furthermore, since demand for standardization of chlorine decay modelling approaches is increasing, it is appropriate to specify main criteria for the selection of chlorine decay models for prediction of chlorine residuals within water distribution networks.

Therefore, the main aim of this research project is to standardize existing and potential future chlorine decay models by introducing practical criteria and evaluate the models against those criteria. This will contribute also to develop better understanding of chlorine decay and formation of disinfectant by-products in water distribution systems which could assist in producing new and more efficient chlorine decay models in the future.

Following the investigation completed by the author on a research project undertaken during a previous master of philosophy study, in this project, initially, reliability of different chlorine decay models for various waters with different qualities will be investigated to determine the model parameters and to observe how various models fit existing measured data. Main drawbacks of the current popular process-based models will be highlighted. Existing models with major weakness will be modified to produce more reliable predictions. Then main criteria for performance improvement of the models will be defined. The nominated chlorine decay models will be compared against some of the defined criteria and the best chlorine decay model will be endorsed. Also, chlorine decay and formation of disinfection by-products in one of the water distribution system in Western Australia will be modelled as a case study. In fact, using the selected model, chlorine decay and formation of DBPs in critical points of this pilot distribution system will be predicted and compared with actual measured values.

The thesis consists of ten chapters. In chapter 1, a brief description of the research background and the overall objectives of the research are given. Chapter 2 provides a comprehensive literature review about all aspects of chlorine decay modelling and its background. Chapter 3 provides information on the methodology and analytical methods for conducting laboratory experiments and performing chlorine decay analysis. In Chapter 4, a new model will be developed to improve the parallel first order model (PFOM). The new model, which is called the modified parallel first order model (MPFOM), will be compared with PFOM. Similarly, In Chapter 5, new model will be developed based on the extended second order model (ESOM) and will be referred to as the modified second order model (MSOM). ESOM will be replaced by MSOM for the remaining of the research study. Chapter 6 discusses the most practical criteria for the selection of mathematical chlorine decay models which are important for effective planning and management of disinfection in complex water distribution systems. Chapter 7 compares the accuracy of the results of the nominated chlorine decay models for single chlorine dosing scenarios. In Chapter 8, the models will be compared for the accuracy of their results for the multiple chlorine dosing scenarios. Chapter 9 compares two of the most accurate models for prediction of chlorine decay in high temperatures. In Chapter 10, chlorine decay and formation of disinfection by-products in one of the water distribution systems in Western Australia will be modelled as a case study using the selected model as the most effective model amongst all nominated chlorine decay models. And, Chapter 11 concludes the dissertation with summary of findings and provides recommendations for future research.

1.2. Research gap, innovation and brief methodology:

As mentioned earlier, over years, many chlorine decay models have been proposed by several researchers. The proposed models in the literature cover a broad range of different modelling approaches; from empirical chlorine decay models to theoretical models. Empirical models are based on hypothetical relationships between chlorine concentration in water and other nominated influencing factors such initial chlorine concentration, pH of water, dissolved organic carbon (DOC), temperature, etc. with time. Theoretical models, on the other hand, define the chlorine decay as function of time using a set of dynamic process equations. These dynamic process equations are however related to physical and chemical principles such as conservation of mass between water and chemical constituents and therefore depend on kinetics of chemical reactions between chlorine and other constituents in water.

Almost all of the researchers who proposed the existing chlorine decay models in the literature claim and provide evidences that their models are amongst the most efficient chlorine decay models. However, there have been many debates and discussions between researchers and scientists about preference of some models over others. In addition, there is a growing demand amongst water utility operators and water quality auditors to seek and find more efficient chlorine decay modelling approaches which can address both planning and management applications. Therefore, an urgent need to standardize the existing chlorine decay models and propose a capable and competent method for evaluating the chlorine decay models has been recognized.

In order to provide meaningful mechanisms for evaluation of chlorine decay models, initially, the most important requirements for modelling chlorine decay need to be investigated. This step requires extensive experience in operation of water networks, water treatment facilities and water quality improvement programs. Also, having technical discussions with water utility operators and also reviewing relevant information in the literature can assist find the most prominent requirements and criteria for modelling chlorine decay in water distribution systems. This step leads to defining a general matrix of criteria for modelling chlorine decay.

The next step for providing an efficient evaluation system for managing the performance of existing and future chlorine decay models is to understand, in details, the advantages and disadvantages of the existing models when compared with the defined criteria. Access to defined performance criteria would enable the researchers and water utility authorities to improve the performance of existing models and could potentially assist propose new chlorine decay models which would generate better results. After defining the practical performance criteria for modelling chlorine decay in water distribution systems, another step is to nominate the most efficient chlorine decay models and assess their performance against the defined criteria. And finally, the best performing model shall be tested for modelling chlorine decay in an actual water distribution system.

Whilst evaluation of one nominated chlorine decay model against another model or performance assessment of the results of a chlorine decay modelling approach against one criteria (mostly accuracy of the results at one condition) has been tried by several researchers, proposing an integrated method to evaluate the performance of various chlorine decay models against a matrix of well researched criteria has not been yet undertaken. Therefore, the current research will potentially make significant contribution to the area of chlorine decay modelling within water distribution systems.

In addition, in an attempt for rectifying the defects of existing models, during the course of this research, two new chlorine decay models will be proposed and will be evaluated against the defined criteria. This also will be considered as significant achievement which can add value to the novelty of the current research work.

1.3. The objectives of the research

The overall goal of this research is to investigate the strength and also weaknesses of existing chlorine decay models and define the required criteria for chlorine modelling in water distribution system. This will help researchers and water utility experts select the most effective model for prediction of chlorine decay in distribution systems.

The Objectives of this research are:

- To establish a comprehensive understanding of various chlorine decay modelling approaches and their strength and weaknesses.
- To define a matrix of criteria for chlorine decay modelling and THM formation in distribution systems.
- To improve or modify existing chlorine decay models in order to make the models achieve better results in prediction of chlorine residuals within water distribution system.
- To compare the capabilities of existing chlorine models and select the most effective modelling approach for prediction of chlorine residuals in the water

distribution network based on the defined criteria.

- To examine the selected chlorine decay model by performing chlorine decay modelling in an actual water distribution system as a case study.

2. Literature Review

2.1. Introduction

Access to adequate and safe drinking water has always been one of the main factors for sustaining the life and development of human civilization. During the history of mankind, major civilizations have been developed around the land areas where access to water for drinking and farming purposes was made available. Indisputably, availability of adequate and safe drinking water supply has always been one of the main factors which impact development of human civilization. Initially, during early stages of this development, quantity of water resources was the main concern for the human being. However, over time, the primary concern with regards to water supply has gradually changed from quantity of water sources to water quality.

The quantity of existing freshwater resources has been reduced greatly due to population growth and extraction of high quality surface waters. Moreover, quality of most remaining fresh water resources has been degraded as a result of these resources being contaminated with municipal, agricultural and industrial wastes.

At the same time, more water quality related diseases have been discovered. This has resulted in considerable increase in general public awareness on water quality issues, leading to water quality regulations being more stringent. In fact, the importance of water quality is now becoming more vital and more focus is being placed on drinking water quality around the world. Therefore, water quality issues can no longer be ignored.

In order to address water quality issues, water from various water resources need to go through some sort of treatment before treated water can reach the consumer. The main treatment processes to remove the containments and improve water quality are similar all around the world. There is a wide variety of water treatment processes available to improve the water quality. However, the choice of treatment process depends on specific water characteristics, types of water quality issues and also cost of treatment process. The following are the most commonly used stages of water treatment process:

- Coagulation
- Flocculation
- Sedimentation
- Filtration

- Disinfection

Usually the last stage of most water treatment processes is disinfection. During this stage, water is disinfected to remove any pathogens that are present in the water and to stop their regrowth in the distribution system. Without disinfection, risk of water quality related disease may be significantly increased.

The main common methods for water disinfection are oxidation using chemicals such as ozone, chlorine or chloramine or removal of microorganisms using ultra-violet (UV) radiation. Chlorination, chloriamination and ozonation are the most commonly used chemical disinfection methods in Australia.

In summary, one of the following disinfection systems may be used in the last stage of a water treatment process:

- Chlorine Disinfection (Chlorination)
- Chloramine Disinfection (Chloramination)
- Chlorine Dioxide Disinfection
- Ozone Disinfection (Ozonation)
- Ultraviolet Disinfection

Disinfection using chlorine (chlorination) appears to be one of the most commonly employed methods for water disinfection around the world. In most water treatment plants, chlorine is usually applied at the end of treatment process as a disinfectant due to its relatively low cost, its effectiveness in removing pathogenic microorganisms and also the ability to provide a residual chlorine concentration in the water distribution system that protects the network against bacterial regrowth.

In this chapter, the history of chlorine disinfection and basic chlorine chemistry will initially be discussed. Then, basic requirements for effective chlorination will be explained and finally history of chlorine decay modelling in water distribution systems and the most popular existing chlorine decay models will be characterized. It is acknowledged that some parts of the Author’s master thesis, which was conducted on the same topic, were cited in this chapter.

2.2. History Overview of Chlorine Disinfection

Before chlorine was used as disinfectant for drinking water treatment, many people used to die due to water related diseases across United States. Typhoid fever was reported to kill around 25 people out of 100,000 people in the US annually. This is nearly the same annual death rate associated with car accidents that are currently occurring in the US.

Over time, however, guidelines have been developed for application of chlorine for water treatment. Also, continual research and development have been undertaken to improve understanding of the chlorination process and its advantages and disadvantages.

Chlorine was first used by John Snow for disinfecting the Broad Street Pump water supply in London after an outbreak of cholera. Later on, in 1897, following a typhoid outbreak, bleach solution was used to temporarily disinfect the water network at Maidstone, Kent in England.

During 1890's, it was the first time that chlorine was applied to water treatment in a water treatment facility in England. At the time, application of chlorine within the treatment plant reduced the number of deaths due to typhoid outbreak. Later, in 1908, chlorine disinfection of water supply was commenced in Jersey City, New Jersey in United States. After this time, almost all cities and towns in the US started to adopt chlorination as part of water treatment process to eliminate deadly water borne diseases including cholera, typhoid, dysentery and hepatitis A. By the end of World War II, chlorination became one of standard methods for water disinfection worldwide.

The use of chlorine in drinking water appears to be one of the most desirable outcomes and the greatest achievements to control widespread prevalence of the waterborne diseases during last century. Therefore, until 1974, adoption of chlorine as the main disinfectant of choice for water treatment was remained unarguable. However, detection of carcinogenic disinfection by-products (DBPs) such as chloroform, around late 1970s, provided an opportunity to raise questions about increasing use of chlorine for water disinfection. In 1974, independent research by Rook and Bellar et al. (1974) confirmed that chloroform can be produced in chlorinated drinking water. Since then, many research activities have been focused on how DBP is formed, its health impacts and the control methods.

However, chlorine is still commonly used as an effective disinfecting agent as it is very powerful, cheap, easy-to-use disinfectant and it has a reasonably long-lasting residual within the water distribution systems (Brown et al. 2011, Freese and Nozaic 2004; Sadiq and Rodriguez 2004; Warton et al. 2006).

2.3. Basic Chlorine Chemistry

Chlorine as disinfectant is usually applied at the end of treatment process. Chlorine is added to water in the form of pressurized gas, which will be dissolved in water at the injection point, or as chlorine solutions (aqueous chlorine) of either sodium hypochlorite or calcium hypochlorite (solid form). Gaseous chlorine (Cl_2) in water hydrolyzes very rapidly to form chlorine ion (Cl^-), hypochlorous acid ($HOCl$) and hydrogen ion (H^+):

$$Cl_2 + H_2O \leftrightharpoons HOCl + Cl^- + H^+ \qquad (2.1)$$

Sodium hypochlorite in water dissociates to yield sodium ion (Na^+) and hypochlorite ion (OCl^-):

$$\mathrm{NaOCl} + H_2O \leftrightharpoons H_2O + Na^+ + OCl^- \qquad (2.2)$$

The solid from of chlorine agent, calcium hypochlorite (which is also known as chlorine powder or bleach powder) will hydrolyze in water to produce calcium ion (Ca^+), hydroxide ion (OH^-) and hypochlorous acid ($HOCl$):

$$\mathrm{Ca}(OCl)_2 + 2H_2O \leftrightharpoons Ca^+ + 2OH^- + 2HOCl \qquad (2.3)$$

In equations 2.1 and 2.3, hypochlorous acid will also hydrolyze to from hydrogen ion and hypochlorite ion:

$$HOCl \leftrightharpoons H^+ + OCl^- \qquad (2.4)$$

Dissociation of $HOCl$ into H^+ and OCl^- is reversible and the direction of the reaction depends on pH and the temperature. This means that distribution of chlorine into $HOCl$ and OCl^- is pH dependant.

When pH values are low, more hydrogen and hypochlorite ions will be combined to form hypochlorous acid. In other words, lower pH values cause the reaction to proceed towards the left. In contrast, high pH will favour formation of the hypochlorite ion and encourages the reaction to occur predominantly from left to the right side. For instance, at pH 5.0 and temperature of 20 °C, more than 99% of free chlorine will be in the form of $HOCl$ and less than 1% in the form of OCl^-. However, when pH is around 8, at the same temperature, only around 23% of free chlorine will be $HOCl$ (Brown, 2011).

Outer surface of pathogens is usually negatively charged. Therefore, they are chemically more attracted to electrically neutral $HOCl$ than the negatively charged OCl^-. Consequently, most pathogens are more susceptible when in contact with $HOCl$ than OCl^-. In fact, $HOCl$ is almost eighty times stronger than OCl^- in deactivating the pathogens (White, 1974).

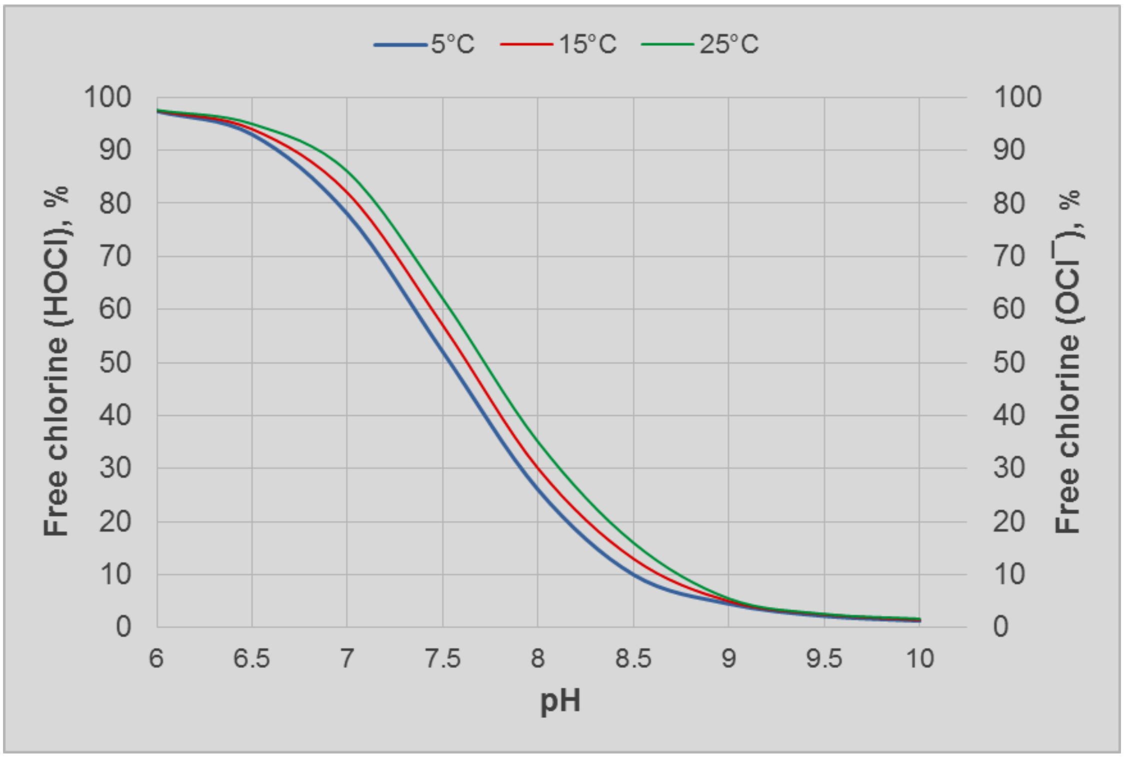


Fig.2.1.*: *Distribution of hypochlorite ion and hypochlorous acid as function of pH and temperature (5°C, 15°C, 25°C); (Brown, 2011)

2.3.1. Free, Combined and Total Chlorine

“Free chlorine” is a term considered for the portion of chlorine in aqueous solution which is formed as hypochlorous acid or hypochlorite ion. Therefore, free chlorine includes the forms of chlorine that has not reacted with other substances in water.

The product of reaction between free chlorine and ammonia or other nitrogenous compounds (organic nitrogen) is called “combined chlorine”. “Total chlorine” is the summation of free and combined chlorine.

When ammonia (NH_3) exists in chlorinated water, hypochlorous acid reacts very fast with ammonia to form chloramines. There are three types of chloramines: monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (nitrogen trichloride; NCl_3). The following equation shows the reaction between hypochlorous acid and ammonia to produce monochloramine:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \tag{2.5}$$

Following the formation of monochloramine, if certain conditions are met, monochloramine will react with remaining $HOCl$ to form dichloramine:

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{2.6}$$

Finally, dichloramine can react with rest of $HOCl$ to produce trichloraine

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{2.7}$$

Occurrence of the above reactions depends on pH, the ratio of concentration of hypochlorous acid to ammonia, the temperature and the reaction time. Monochloramine is usually formed when pH values are higher than 8. Also, if the molar ratio of hypochlorous acid to ammonia is lower than 1.0, monochloramine is mainly produced. Other forms of chloramines, i.e. dicholamine and trichloramine, are formed when chlorine-to-ammonia ratio is greater than 1.0 or at lower pH values. When pH is less than 3, trichloramine is the only chloramine species that can usually be detected (Morris, 1978b; Deborde and vun Gunten, 2007).

Combined chlorine, such as monochloramine (NH_2Cl), has much weaker disinfectant characteristics compared to free chlorine. Since total chlorine is the combination of free and combined chlorine, it provides the total disinfection potential for a water sample.

2.3.2. Chlorine Reaction with Organic and Inorganic Compounds

Chlorine is a powerful disinfectant and has strong reaction properties. Therefore, it reacts with many organic and inorganic elements in water. Reaction mechanisms between chlorine and most of inorganic compounds are well understood. However, reaction pathways for chlorine reaction with inorganic substances are still relatively unknown due to the site specific and heterogeneous nature of the natural organic matters (Boccelli et al., 2003).

Generally, the following reaction pathways can occur during reactions between aqueous chlorine and organic and inorganic compounds:

- Oxidation reaction
- Addition reaction
- Substitution reaction
- Light decomposition reaction

Reaction between chlorine and inorganic substances such as manganese (Mn^{2+}), iron (Fe^{2+}), ammonia (NH_3) and Halides (SO_3^{2-}, CN^- or sulfide) occurs as result of oxidation process. During oxidation process, the positively charged part of the strongly polarized $Cl-O$ bond in hypochlorous acid or hypochlorite ion forces the inorganic substance to release and transfer electron, thus oxidizing the inorganic matter. Oxidation reactions between chlorine and inorganic matters usually occur very fast.

The following are some examples of oxidation reactions between chlorine and inorganic substances in water (Gang et al., 2003):

$$\mathrm{HOCl} + 2\mathrm{Fe}^{2+} \rightarrow 2\mathrm{Fe}^{3+} + \mathrm{Cl}^- + \mathrm{OH}^- \quad (2.8)$$

$$\mathrm{HOCl} + \mathrm{Mn}^{2+} \rightarrow \mathrm{Mn}^{4+} + \mathrm{Cl}^- + \mathrm{OH}^- \quad (2.9)$$

$$4\mathrm{HOCl} + \mathrm{S}^{2-} \rightarrow \mathrm{SO}_4^{2-} + 4\mathrm{Cl}^- + 4\mathrm{H}^+ \quad (2.10)$$

$$\mathrm{HOCl} + \mathrm{Br}^- \rightarrow \mathrm{HOBr} + \mathrm{Cl}^- \quad (2.11)$$

$$3\mathrm{HOCl} + 2\mathrm{NH}_3 \rightarrow \mathrm{N}_2 + 3\mathrm{Cl}^- + 3\mathrm{H}_2\mathrm{O} + 3\mathrm{H}^+ \quad (2.12)$$

The chemical structure and pathways of chlorine reactions with organic compounds are, however, more complicated. Reaction between chlorine and organic matters can occur due to oxidation reactions, addition reactions to unsaturated bonds or electrophilic substitution reactions at nucleophilic sites (Deborde and vun Gunten, 2007).

The following equation provides an example of the oxidation reaction between hypochlorous acid and organic matters:

$$\mathrm{R - CHO + HOCl \rightarrow R - COOH + Cl^{-} + H^{+}} \qquad (2.13)$$

During addition and substitution reactions between chlorine and organic matters, chlorinated organic intermediates will be produced as result of chlorine being added or substituted into the natural organic matter (NOM) molecular structure. The intermediate products may be further decomposed to form other types of disinfection by-products, DBPs (van Hoof, 1992; Gang et al., 2003).

Substitution reactions of chlorine with organic compounds may include a series of parallel and/or serial reactions. Some of these reactions may occur fast and some are slow reactions. Addition and oxidation reactions of chlorine with organic matters are, however, typically slow. Amongst all forms of chlorine reactions with organic matters, only electrophilic attacks of chlorine on the structure of organic compounds can occur fast enough to be significant (Deborde and vun Gunten, 2007).

2.4. Chlorinated Disinfection By-Products

Chlorine reaction with organic and inorganic matters will result in formation of a wide range of intermediate and also inert products. Intermediate products are the ones which further react with chlorine to produce inert products. Inert products are usually the final products of chemical reactions.

Chlorinated disinfection by-products (DPBs), which are also called chlorination by–products, are the inert products of chemical reactions between chlorine and natural organic matters (NOMs) in water. DBPs are therefore the natural result of water disinfection using chlorine. Some DBPs have been found to be carcinogenic and some others are suspected of provoking severe heath issues. Also, some chlorinated by-products have been proved to cause negative reproductive or developmental effects in animal studies.

More than 600 chlorinated DBPs including trihalomethanes (THMs), haloacetic acids (HAAs) and N-Nitrosodimethylamine (NDMAs) have been discovered so far. Whereas trihalomethanes (THMs) have been found in highest extent, NDMAs are discovered to be the most harmful disinfection by-products.

2.5. Advantages and Disadvantages of Chlorination

Chlorination as one of most well-known types of disinfection has the following advantages:

- Chlorine is a very strong disinfectant; therefore, it can control most of pathogenic micro-organisms in water.
- Chlorine is a long lasting disinfectant; therefore, it provides a residual in the distribution system to protect water from re-contamination.
- It has been used for almost more than a century for water disinfection; therefore, it is better understood than other disinfectants.
- The most important part of disinfection that can be achieved by chlorination is to damage the cells of micro-organism which prevents them to multiply and therefore it causes the micro-organisms to die.
- Chlorine also decomposes/destroys some of the organic and inorganic substances in water that are food sources to microorganisms.

Although chlorination is considered to be the most advantageous disinfection method at water treatment plants and distribution systems, it has some disadvantages as well:

- As mentioned earlier, the first issue of chlorination is that chlorine reaction is pH-dependant. As a result, depending on the water pH, various types of free chlorine including HOCl and OCl^- may be formed during disinfection. Different forms of disinfectants have different reactivity strength in deactivating organisms in the water. Therefore, in order to obtain consistent results during laboratory experiments, water pH will have to be monitored carefully. Moreover, lower water pH is more desirable during treatment process, due to the fact that stronger chlorine species such as HOCl will be formed when pH values are lower.
- The second disadvantage of chlorination is that chlorine reaction with Natural Organic Matter (NOM) and inorganic substances in water results in formation of Disinfection By-Products (DBPs). Some of the DBPs are proved to be carcinogenic and harmful to human health. Though most types of disinfectants will produce some sorts of harmful by-products, chlorination has found to form more chlorinated by-products.

2.6. Basic Requirements for Effective Chlorination (Chlorination Goals)

As mentioned earlier, the main objective for using chlorine as disinfectant in water treatment is to terminate microorganisms including bacteria and viruses that are contained in water and are found harmful to human health.

Water disinfection is essential to control micro-organisms that are generally of health concerns to the human. Chlorine, as a cost effective and highly efficient disinfectant, is usually added to water at the final stage of water treatment process. Chlorine is known as a non-selective oxidant which reacts with most organic and inorganic substances in water. Therefore, it functions as a highly effective antimicrobial agent to minimise the risk of water-born and infectious disease (Jabari Kohapei et al., 2010). However, certain requirements have to be met to ensure effective chlorination in removing the harmful pathogens in water is achieved.

2.6.1. Minimum Chlorine Residual (Primary and Secondary Chlorination)

At the point of injection, chlorine starts to react with various substances in water including organic and inorganic matters and also with microorganisms. Chlorine reaction with inorganic substances is almost instantaneous. Reaction with organic matters and microorganisms, however, could take longer depending on the type of organic species and/or microorganisms. There should be sufficient chlorine added to water during disinfection process to achieve adequate inactivation of microorganisms before treated water reaches the customer. This is called primary disinfection.

Moreover, even in chlorinated water, regrowth of microorganism and water re-contamination may occur due to change in the condition of the distribution systems. A minimum concentration of chlorine (chlorine residual) is, therefore, required to always be maintained at all points of the distribution system in order to prevent microbial regrowth. This is referred to secondary disinfection. Consequently, and in accordance with water quality regulations, it is critical to have a minimum chlorine residual over the entire distribution system and at all times. (Jabari Kohapei et al., 2010). The minimum free chlorine residual of 0.2 mg/L within distribution system should be maintained in accordance with Australian Drinking Guideline, 2011.

2.6.2. Minimum Contact Time (CT)

Chlorine disinfection to remove pathogens in water is not instantaneous. In other words, it takes time in order for dangerous microbes, bacteria or viruses in the water to be inactivated by chlorine. Inactivation time for different types of pathogens to be removed varies broadly. Amoebic cysts are generally the most resistant species when exposed to chlorine. Thus, amoebic cysts require more exposure time in contact with chlorine to be inactivated. On the other hand, most bacteria, including Vibrio Cholerae will be destroyed quickly in contact with free chlorine at normal conditions. For instance, in order to remove schistosomiasis cercariae, it needs to be exposed to 1 mg/L of chlorine residual at least 30 minutes. However, 2 mg/L of free chlorine is required to kill amoebic cysts within the same exposure time. Therefore, it is vital to ensure sufficient contact time is available for the free chlorine before water reaches the first customer.

To achieve the required contact time in piped water distribution systems, chlorinated water will be sent into and kept in a storage tank, which is usually called contact tank, for the period of contact time. In small water network, one of main storage tanks can be used as contact tank. In larger systems, however, purpose-built tanks with internal baffles to provide adequate mixing and achieve longer retention time will be used (Fact sheet 2.17, WHO, 1996).

2.6.3. Improving Taste and Odour

High concentration of chorine in drinking water results in taste and odour issues. Although, the concentration limit for chorine itself to cause odour issues is relatively high, these limits for chloramines are significantly lower. Therefore, it is advisable to limit the chlorine demand in drinking water in order to meet aesthetic requirements.

2.6.4. Minimising Disinfection By-Products

As discussed earlier, formation of disinfection by-products (DBPs) is a likely result of reaction between chlorine and natural organic matters (NOMs) and some of these DBPs has been found to be carcinogenic and harmful to human health. Hence, the chlorine concentration should be limited in order to decrease the disinfection by-products formation potential.

2.6.5. Minimising Chlorine Demand

As already pointed out, the main reason for using chlorine as disinfectant is to react with and kill harmful microorganisms, which are potentially the main sources of water-related health issues. However, because of having reasonably high oxidation potential, chlorine also reacts with other organic and inorganic matters in water and therefore decays over time. As a result, more chlorine is usually required than expected to satisfy the primary and secondary disinfection.

The difference between the amount of chlorine that is added to the water and the free chlorine residual is referred to chlorine demand. The higher the chlorine demand is for a water sample, the more is the amount of disinfection by-product produced (Gao et al. 2013). Therefore, minimising chlorine demand should be targeted during water chlorination.

2.7. Methods/Tools for Achieving Effective Chlorination

In order to achieve the chlorination goals, the following methods/tools can be utilized or further investigated:

2.7.1. Enhancement of Water Treatment Process

From above discussion, it can be concluded that enhancement of water quality by improving the treatment process could significantly minimise the chlorine demand and thus results in reduction in DBPs formation. This is simply because more enhanced treatment processes will result in reduction of the concentration of natural organic matter in water. Therefore, it is reasonable to improve the water treatment quality and define a maximum and minimum limit for the chlorine concentration in the water disinfection process.

2.7.2. Modelling Chlorine Decay

As described, controlling chlorine demand in bulk water can be achieved mainly by enhancement of water quality and water treatment processes. However, to achieve secondary disinfection, it is also required that chlorine residuals be monitored during the time water is travelling through entire distribution system. In order to monitor chlorine residuals over the whole network, chlorine decay should be accurately predicted. Prediction of chlorine decay accurately has been found to be a challenge. This is due to the fact that chlorine decay behaviour is considerably influenced by water quality characteristics such as total organic carbon (TOC) or dissolved organic carbon (DOC) and pH of water. Characteristics of the distribution system such as hydraulic and non-hydraulic conditions including retention time and pipe materials and also ambient conditions such as temperature may also have significant impact on chlorine decay profile. (Clark and Sivaganesan, 2002). Therefore, in order to accurately predict chlorine decay behaviour and monitor chlorine residuals over the entire water distribution system, a robust mathematical modelling approach is required (Jabari Kohapei et al., 2010).

2.8. Main Reasons for Modelling Chlorine Decay

One method to determine the adequacy of primary and secondary chlorination throughout water distribution system and to control the side effects of chlorination (i.e. odour and by-product issues) is to know about chlorine decay behaviour and to predict it. However, chlorine decay behaviour has been found to be considerably influenced by water quality characteristics such as total organic carbon (TOC) or dissolved organic carbon (DOC), pH and temperature. There are also several indications of how different types of treatment processes and also various hydraulic and non-hydraulic conditions in the distribution system (such as corrosion, biofilm) may impact the chlorine decay profile (Clark, 2002). Therefore, the chlorine demand, the retention time and its required set point and initial dosing vary from one water source to another, over different water networks or different seasons within the same network (Clark, 2002).

In order to consider all these above-mentioned parameters for prediction of chlorine decay, a robust chlorine decay modelling approach is required. Chlorine decay models are mathematical tools for prediction of chlorine residuals at any location of a water distribution network at any time after initial chlorination or re-chlorination.

2.9. Potential Applications for Modelling Chlorine Decay

In large and complex water distribution systems, mainly, two generic types of applications for chlorine modelling can be considered: management and planning applications.

Management applications are concerned with the evaluation of disinfection performance in existing networks. They also consider the development of alternative approaches to improve performance with little or no change in existing infrastructure. The definition of performance is to achieve desirable or target chlorine concentrations at specified locations within the system. Target concentrations can be defined and set to achieve goals directly addressing the issues raised previously:

- The initial concentration required to achieve the specified concentration-time parameter (Ct) for primary disinfection
- The minimum chlorine residual (concentration) to be maintained at all points in the system to satisfy secondary disinfection
- The maximum concentration to satisfy aesthetic requirements.
- The maximum chlorine concentration due to the limit specified for chlorinated by-products

The goal to set a maximum chlorine for chlorinated by-product formation can be defined in terms of chlorine consumed at the time the water reaches any point of consumption (Clark, 1998), or as the ultimate total accumulated dose.

Alternative improvement strategies/approaches can be evaluated by setting up each possible approach within the model to achieve performance goals for each strategy/approach from model runs. The most acceptable option can then be selected from all approaches considered, before any trial is performed in the real water network. In this type of application, alternative approaches can be stated as to those engaging measures such as diverting flows and changing flows rates, maximum/minimum reservoir levels, and the amount of chlorine doses.

The second type of application in regards to chlorine decay modelling in distribution systems is concerned with planning. With respect to planning application, the same performance measures, strategies and targets apply. However, the scale of alternative improvement approaches is much larger and may include major changes in infrastructure, such as new tanks, pumps, and pipelines or extra chlorine booster stations at appropriate locations. Modification of treatment processes to remove more NOM or inorganic substances, prior to water entering the distribution system, can also be considered as an option. It is apparent that there is no alternative to the modelling approach for planning applications. This is because there is no physical system in which any alternative could be tested, until after a new strategy is identified and implemented.

2.10. Chlorine Bulk Decay vs. Wall Decay

In water distribution systems, chlorine decay occurs due to reaction with substances in water and also as result of interaction between chlorine and the pipe wall. The reaction between chlorine and substances in water is called bulk decay. However, chlorine decay due to its reaction with pipe wall is referred to wall decay.

2.10.1. Chlorine Bulk Decay

It is expected that most chlorine bulk decay occurs during primary chlorination i.e. at the end or during water treatment process, at the beginning of distribution system or immediately after initial chlorination. However, bulk decay may also occur when water travels through the pipes. This is because some reactions between chlorine and the substances in the bulk water continue to occur at slower rate than other chlorine bulk reactions. Another contributing factor for occurrence of bulk decay within water distribution system may be re-chlorination which happens at the chlorine booster stations at the middle of the water network.

Chlorine bulk decay has been found to be best described using the first order kinetics model with respect to initial chlorine concentration (Arevalo, 2007). However, this model has been found to be very simplistic which is site specific, does not represent the bulk decay profile accurately and produces different kinetic constants for different waters (Powell et al., 2000).

2.10.2. Chlorine Wall Decay

Chlorine wall decay consists of various reaction pathways between chlorine and the substances that are attached or incorporated into the pipe wall. This may include corrosive reactions with the pipe wall material itself, with adhering biofilms and with accumulated sediments. Therefore, chlorine wall decay can be defined as a function of the following parameters (Vieira et al. 2004; Warton et al. 2006):

- Mass transfer of chlorine from the bulk water to the pipe wall
- Pipe material
- Pipe diameter
- Pipe age
- Pipe internal coating
- Attached biofilm

2.11. Separation of Bulk and Wall Decay Mechanism

Although, in reality, bulk and wall chlorine reaction occurs simultaneously, separating these two phenomena makes chlorine decay modelling much easier. Vasconcelos et al. (1996) showed that the wall decay can be considered as the difference between the chlorine concentrations at key locations of the water network estimated from modelling the bulk decay, and the values of the chlorine residuals measured at the corresponding locations in the real system. Figure 2.2 illustrates the relationship between the bulk and wall decay as discussed by Vasconcelos et al. (1996).

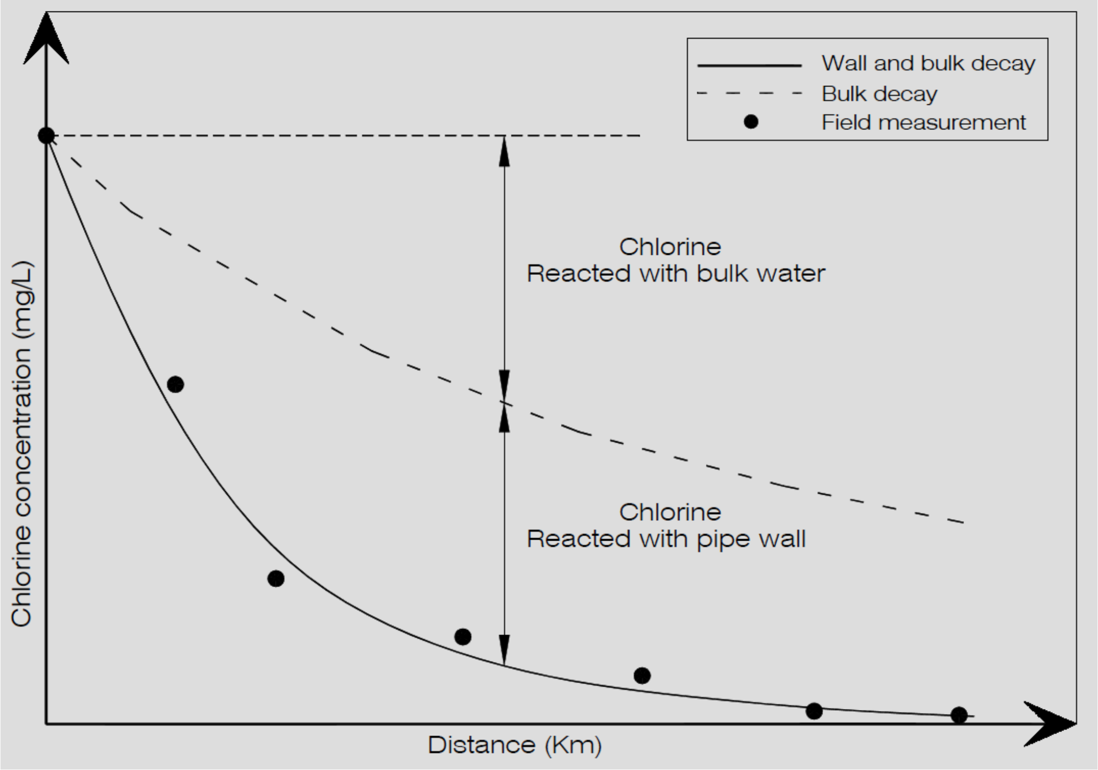


***Fig.2.2.*: Conceptual separation between bulk and wall decay of chlorine in a water network pipeline**

The most popular chlorine decay model is the first order model which is a simple exponential reduction of chlorine concentration with time. The first order model has only one parameter/coefficient to be estimated/determined using lab testing and field measurements. Even using the first order chlorine decay model, with only one parameter/coefficient, major effort and cost would be involved in calibrating this single parameter/coefficient, to match lab/field measurements at key locations throughout a complex system (Vasconcelos et al., 1996). If the bulk decay is modelled separately from the wall decay, changes to the system (e.g., pipe cleaning programs, rerouting water and renewing pipes, especially with different materials, or adding new ones) should require only the wall decay in those altered parts of the system to be recalibrated.

Moreover, practical experience has also proved that extensive recalibration is required when source water characteristics, water temperature and/or initial or booster chlorine concentration change. Similarly, if the bulk decay characteristics is separated from the wall decay mechanisms, then only recalibration of the bulk decay should be required when such changes occur.

Therefore, it is deemed an appropriate consideration to model chlorine reaction with substances in water (termed bulk decay) independently from the decay due to chlorine interaction with other particles/material adhered/deposited to or separated from pipe wall (termed wall decay).

It should be noted, however, that there are circumstances under which this separation is not valid. In iron pipe systems with no internal lining, some of corrosion products from the pipe wall may be released and mixed into the bulk flow when the flow velocity becomes high enough. However, Clark and Haught (2005), in a laboratory pilot pipe-loop experiment, demonstrated that turbidity due to the corrosion of a 150mm diameter tuberculated pipe is not affected until the flow velocity does not exceed 200mm/s. As a result, the separation of bulk from wall decay may still be valid in many systems of unlined pipes.

Another condition under which chlorine bulk decay may be influenced by wall characteristics is when biofilm is sloughed from the pipe wall and reacts with chlorine contained in the bulk water flow, increasing the bulk decay reaction rate. However, biofilm usually develops on the internal surface of the pipe wall over the long period, withstanding the range of normal changes of the flow in the pipe. In order for the biofilm to detach from the pipe wall, therefore, an unusual flow change needs to occur. Hence, the occurrence of biofilm sloughing from the pipe wall affecting the bulk decay can be considered unlikely in normal pipe systems and consequently the chlorine demand of biofilm can be assumed as part of the wall reaction and independent from the bulk decay (Fisher et al., 2011).

2.12. Data-Based (Empirical) and Process-Based (Theoretical) Modelling Approaches

In order to achieve chlorination goals by enhancement of the performance of the chlorine decay modelling approach, the decay model must be able to estimate chlorine residuals at any location of interest in the distribution system, using the initial chlorine concentration applied at the treatment plant. The model must also explicitly or implicitly account for the effect on residual of time of travel to key locations since these times may differ substantially in different seasons and between various approaches in the same season (Fisher et al., 2011). There are two major categories of chlorine decay models which have these capabilities: the data-based (or empirical) models and the process-based (or theoretical) models.

Data-based or empirical models are essentially based on a hypothetical relationship between chlorine concentration in water and other nominated influencing factors such initial chlorine concentration, pH of water, dissolved organic carbon (DOC), temperature, etc. with time.

One of the recent examples of the data-based approaches for the chlorine decay models is artificial neural network (ANN) model. ANN is a computational model based on the structure and functions of biological neural networks. Information that flows through the network affects the structure of the ANN because a neural network changes - or learns, in a sense - based on that input and output.

ANN models require broad data sets containing the range of conditions under which the system is to be operated. These models require development of a complex connection between inputs and outputs (residuals at key locations). For instance, ANN models have been utilised to model free chlorine and trihalomethane (THM) formation in distribution systems (Rodriguez et al., 1997).

As long as the data sets from which the model is derived cover the range of conditions to be explored by alternative management strategies, ANN models can be satisfactory for management applications. However, even the alternative strategy of rerouting some of the water would not be adequately represented by an ANN model, unless this had already occurred for some of the time in the training data set. By definition, this condition is not met in planning applications because the system to be modelled does not exist at the time of planning. Consequently, no data-based models of chlorine decay (including ANN models) are usable for planning applications.

Mechanistic or process-based models are usually defined with two sets of equations and associated variables. One of these sets of equations/variables describes the effects of system hydraulics on chlorine demand and the other is based on chemical reactions between chlorine and other substances. These equations and variables are related through physical and chemical principles including conservation of mass for water and chemical constituents and kinetics of chemical reactions. To obtain the time-varying concentrations of chlorine and the values of other variables, the equations are to be solved. The solution for time-varying hydraulic variables such as flows in fact provides the time that is required for chemical reactions to occur within each parcel of water whilst it travels through the system. This allows the time-varying chlorine residuals to be determined from these reactions at any point in the system.

Some of the equations within process-based models are called process equations. These equations comprise parameters or coefficients whose values have to be estimated using appropriate experimental data or by undertaking in-system measurements.

Process-based models are useful for both management and planning applications. In planning applications, due to the fact that the system of interest does not yet exist, the values of the model parameters may be derived from other similar systems. The estimated values in process-based models are more likely to be appropriate than those obtained in the data-based ones, where no physical or chemical interpretation of the parameters is available. As a result, the focus of this research will be on assessment of process-based models and less emphasis will be placed on data-based models.

2.13. Chlorine Bulk Decay Models

To date, several empirical and theoretical models have been developed for prediction of chlorine decay in bulk water. As discussed, empirical models are based on relationship between chlorine consumption and certain water characteristics such as TOC, DOC, pH and temperature. On the other hand, theoretical models define the chlorine decay as function of time using a set of dynamic process equations. These dynamic process equations are however related to physical and chemical principles such as conservation of mass between water and chemical constituents and also depend on mass-action kinetics in chemical reactions. Theoretical models have been shown to be more suitable for both planning and management applications than empirical models (Fisher et al., 2010a). Therefore, theoretical chlorine decay models, which are based on the chemical reactions between chlorine and various constituents in the water, have been paid more attention in the literature.

2.13.1. Empirical (Data Based) Chlorine Decay Models

As discussed earlier, empirical models are considered the models which are based on relationships between chlorine consumption and certain water quality properties such as TOC, DOC, pH and temperature. The following are the main popular empirical chlorine decay models within the literature:

2.13.1.1. Feben and Taras (1951) Model:

Feben and Taras (1951) developed a simple empirical equation for prediction of chlorine bulk decay in drinking water. Their model is possibly one of the earliest chlorine decay models which directly relates the loss of free chlorine concentration to the power function of time:

$$\mathrm{D_t} = D_1\mathrm{t^n} \qquad (2.14)$$

Feben and Taras defined their model variables as below:

$\mathrm{D_t}$ is the chlorine concentration which is consumed in parts per million at the end of contact time t, $D_1$is the amount of chlorine consumed after one hour from initial dosing and n is exponential constant to be estimated by experiment.

Feben and Taras model equation can be re-arranged as below:

$$\mathrm{Cl_t} = \mathrm{Cl_0} - \mathrm{kt^n} \qquad (2.15)$$

where $\mathrm{Cl_t}$ is the concentration of chlorine residual [mg/L] at time t[h], $\mathrm{Cl_0}$ is the initial chlorine concentration and k and n are parameters that need to be estimated for data fitting.

Feben and Taras model needs more than one set of parameters to be estimated in order to fit the data over the entire contact time. Below are some of the disadvantages of their model:

- The power n is limited to the values between 0 and 1.
- As time t increases, the values for chlorine concentration can turn negative instead of asymptoting towards zero.
- Feben and Taras (1951) model is not based on the water characteristics. The model does not also relate to chemical kinetics of chlorine reactions. Therefore, this model has not been developed further to be used as a popular chlorine modelling approach.

2.13.1.2. Lyn and Taylor (1993) Model:

Lyn and Taylor (1993) proposed an empirical function to predict the chlorine residual of a particular treated water based on chlorine dose, DOC, temperature and time:

$$\mathrm{Cl(t)} = 0.285\mathrm{Cl}_0^{1.631} + \mathrm{DOC}^{-0.313}\mathrm{T}^{-0.176} - \mathrm{DOC}^{-0.241}\mathrm{T}^{0.101}\mathrm{t}^{0.265} \qquad (2.16)$$

where Cl_0 is the initial chlorine concentration, DOC is dissolved organic carbon, T is temperature and t is the contact time.

Lyn and Taylor model describes the entire chlorine reaction with all substances in a water sample which is treated in a particular water treatment plant using a particular ground water source. In fact, all parameters associated with their model may only suit the water for which they did the experiments.

Another disadvantage of the Lyn and Taylor mode is that, similar to Feben and Taras (1951) model, their model may predict negative values for the chlorine concentration.

2.13.1.3. Dugan et al. (1995) Model:

Based on the Michaelis-Menten equation, Dugan et al. (1995) developed a saturation type model for describing the entire chlorine decay curve with a single equation:

$$\frac{\mathrm{dC}_t}{\mathrm{dt}} = \frac{-\mathrm{k} \times \mathrm{TOC} \times \mathrm{C_t}}{\mathrm{K} \times \mathrm{TOC} + \mathrm{C_t}} \qquad (2.17)$$

where $\mathrm{C_t}$ is chlorine concentration at time t and K and k are rate constants for which two empirical relationships with $\mathrm{C_0}$ and TOC were established.

$$-\mathrm{K} = 0.85 \times \left(\frac{C_0}{TOC}\right) \qquad r^2 = 0.93 \qquad (2.18)$$

$$-\mathrm{k} = 0.03 - 0.006 \times \left(\frac{C_0}{TOC}\right) \qquad r^2 = 0.21 \qquad (2.19)$$

where $\left(\frac{C_0}{TOC}\right)$ is the ratio between initial chlorine concentration and the amount of total organic carbon (TOC) of the water.

The saturation model developed by Dugan et al. (1995) was able to predict chlorine decay accurately in untreated waters with low to moderate TOC concentrations. However, the model could not estimate the chlorine residual concentrations well for ground waters at lower concentrations or for treated waters (Koechling, 1998).

2.13.1.4. *Koechling (1998) Model:*

Koechling (1998) modified the saturation type model developed by Dugan et al. (1995) based on the Michaelis-Menten equation. Koechling (1998) assumed a generalized model as below:

$$\frac{\mathrm{dC}_t}{\mathrm{dt}} = \frac{-\alpha_2 \times \mathrm{C_t}}{\alpha_1 + \mathrm{C_t}} \tag{2.20}$$

with α_1 and α_2 representing kinetic rate constants.

Koechling (1998) then investigated the dependence of kinetic constants on water quality parameters by plotting α_1 and α_2 against certain water quality parameters. Multiple linear and non-linear regressions using various water quality parameters were performed in order to investigate whether predictive relationships exist between α_1 and α_2 and water quality parameters. Eventually, the following equations were proposed and tested by Koechling to predict the chlorine residual concentrations for various waters:

$$\frac{\mathrm{dC}}{\mathrm{dt}} = \frac{-\mathrm{k_2} \times \mathrm{SUVA_0} \times \mathrm{C_t}}{\alpha_1 + \mathrm{C_t}} \tag{2.21}$$

where $\mathrm{k_2}$ is the rate parameter and $\mathrm{SUVA_0}$ is the initial specific ultraviolet absorbance at a wavelength of 254nm.

Integrating the above equation yileds:

$$\mathrm{C_t} = \alpha_1 \times \ln(\mathrm{C_0}/\mathrm{C_t}) - \mathrm{k_2} \times \mathrm{SUVA_0} \times \mathrm{t} + \mathrm{C_0} \tag{2.22}$$

Koechling also developed predictive relationships for $\alpha_1$and $\mathrm{k_2}$ at $\frac{\mathrm{CL_2}}{\mathrm{DOC}} = 2$ as below:

$$\alpha_1 = 4.98 \times \mathrm{UAV_0} - 1.91 \times \mathrm{DOC} \qquad r^2 = 0.99 \tag{2.23}$$

$$\mathrm{k_2} = -0.32 \times \mathrm{UAV_0}^{\;1.365} \qquad r^2 = 0.882 \tag{2.24}$$

2.13.2. Theoretical (Process Based) Chlorine Decay Models

As explained earlier, theoretical (process based) chlorine decay models are typically based on the chemical reactions which could potentially occur between chlorine and various substances in water. Most of chlorine is depleted in water due to partial oxidation of natural organic matters (NOM) to form inert products. It has been found that most of these reactions are in the form of parallel chemical reactions between chlorine and NOMs contained in water (Deborde and vun Gunten, 2007). Minor fraction of chlorine may take part in oxidation of organic matters to produce DBPs. The reactions between chlorine and NOM which lead in formation of DBPs might be in the form of serial, parallel or complex pathways (Deborde and vun Gunten, 2007; Kastl et al., 1999).

Consequently, it is reasonable to assume that chlorine depletes in bulk water via a series of simultaneous parallel and serial reaction with many different substances in water. Ignoring the serial reactions between chlorine and constituents in water and assuming that all chlorine reaction with aqueous substances are in the parallel format, each reaction between chlorine and various compounds in water can be typically expressed as follows:

$$\mathrm{Cl} + \mathrm{X_i} \overset{\mathrm{k_i}}{\rightarrow} \mathrm{P_i} \qquad (2.25)$$

where Cl represents chlorine, $\mathrm{X_i}$ is represents the typical aqueous substance or a molecular site of a complex compound in water that reacts with chlorine, ki is the rate constant and $\mathrm{P_i}$ is the product of the reaction.

Assuming that chlorine decay in water occurs due to n parallel reactions, and that all reactions are first order with respect to the reactants and second order overall, the overall rate for each typical reaction can be defined as below:

$$\frac{\mathrm{dC_{Cl}}}{\mathrm{dt}} = -\mathrm{C_{Cl}} * \sum_{i=1}^{n} \mathrm{k_i} * \mathrm{X_i} \qquad (2.26)$$

where $\mathrm{C_{Cl}}$ is the chlorine concentration at time t, $\mathrm{X_i}$ is the concentration of ith aqueous substance in water reacting with chlorine at time t and $\mathrm{k_i}$ is its corresponding reaction rate constant.

Jonkergouw et al. (2009) proposed a variable rate coefficient chlorine decay model in order to consider all above mentioned reaction pathways. They defined a new parameter referred to as the concentration-weighted average rate coefficient for the entire set of reactions occurring between chlorine and other reactants in water.

$$\kappa_t = \frac{\sum_{i=1}^{n} \mathrm{k_i} * \mathrm{X_{i,t}}}{\mathrm{X_t}} \qquad (2.27)$$

$$\mathrm{X_t} = \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{X_{i,t}} \tag{2.28}$$

$$\frac{\mathrm{dC_{Cl}}}{\mathrm{dt}} = \frac{\mathrm{dX_t}}{\mathrm{dt}} = -\kappa_\mathrm{t}\mathrm{X_t}\mathrm{C_{Cl}} \tag{2.29}$$

where $\mathrm{X_{i,t}}$ is the concentration of each reactant at time t, $\mathrm{X_t}$ is the sum of their concentrations and κ_t is the new term defiend as the concentration-weighted average rate coefficient for all reactions.

Jonkergouw et al. (2009) confirmed that there is no analytical solution for equation 2.27. Therefore, they proposed an empirical equation for κ_t with similar mathematical behaviour:

$$\frac{\mathrm{d}\kappa_\mathrm{t}}{\mathrm{dt}} = aC_{Cl}(\kappa_\mathrm{t}k_{min} - \kappa_\mathrm{t}{}^2) \tag{2.30}$$

where a is a positive dimensionless coefficient and k_{min} is the minimum value of κ_t.

The variable rate chlorine decay model is shown to be of high accuracy in prediction of chlorine residuals for various bulk decay tests (Jonkergouw et al., 2009). However, the efficiency of this model in comparison with its complexity is being questioned. The most important disadvantage of Jonkergouw et al. (2009) is that it would not be acceptable to formulate all reactions between chlorine and other reactants in water without indicating their decay properties (Fisher et al., 2009).

In addition, as mentioned earlier, depending on type and amount (concentration) of the substances reacting with chlorine, the nature of their reactions and the magnitude of the rate constants, numerous number of various parallel reactions between chlorine and the substances in water might occur simultaneously or consecutively. Therefore, it is impractical to consider and analyse all these reactions with chlorine using a chlorine decay modelling approach even if all reaction characteristics were known (Jabari Kohpaei et al., 2010).

Most theoretical (process based) chlorine decay models, therefore, assume that all these parallel reactions occurring between chlorine and other substances in bulk water can generally be described using one or two reactions.

2.13.2.1. *First Order Model (FOM):*

In the beginning, one of the simplest and most common and popular theoretical (process based) chlorine decay models for modelling chlorine decay in bulk water has been the first order model (FOM). Based on first order kinetics, only one component is involved in the reaction scheme; i.e. compound A is converted to compound B (A→B). In fact, the reaction rate for FOM is only proportionate to the first power of the concentration of the reactant. Using first order kinetics, chlorine concentration is assumed to be decreased over time by itself. In other words, FOM does not take into account the effect of other species with which chlorine is reacting. The general first order kinetic expressions for chlorine decay model in bulk water is as follows:

$$\frac{\mathrm{dCl}}{\mathrm{dt}} = -\mathrm{k} * \mathrm{Cl} \tag{2.31}$$

$$\mathrm{Cl(t)} = \mathrm{Cl_0} \exp(-\mathrm{kt}) \tag{2.32}$$

where $\mathrm{Cl(t)}$ is chlorine concentration at time t, $\mathrm{Cl_0}$ is initial chlorine concentration [mg/L] and k is the decay constant [h-1].

Figure 2.3 shows a typical chlorine decay profile of a chlorinated water sample taken from effluent of a water treatment plant. The polyline connecting the measured data points on Figure 2.3 shows the general trend of chlorine decay behaviour that could be seen for most chlorinated drinking water samples. As can be seen from the figure, a sharp decline in free chlorine decay occurs immediately after chlorine dosing. This is followed by a much more gradual decline afterwards.

Figure 2.3 also shows the predicted chlorine decay line using FOM for the selected data. It is clearly shown that FOM cannot predict the initial higher decay rate followed by much slower reaction rate.

If FOM was able to accurately model the chlorine decay behaviour, the line corresponding to the actual (measured) decay data would be a horizontal straight line in a semi-log plot. Obviously, this is not the case, i.e. the decay rate is very high initially to reach a turning point and then continues to fall much more slowly thereafter. (Fisher et al., 2010a).

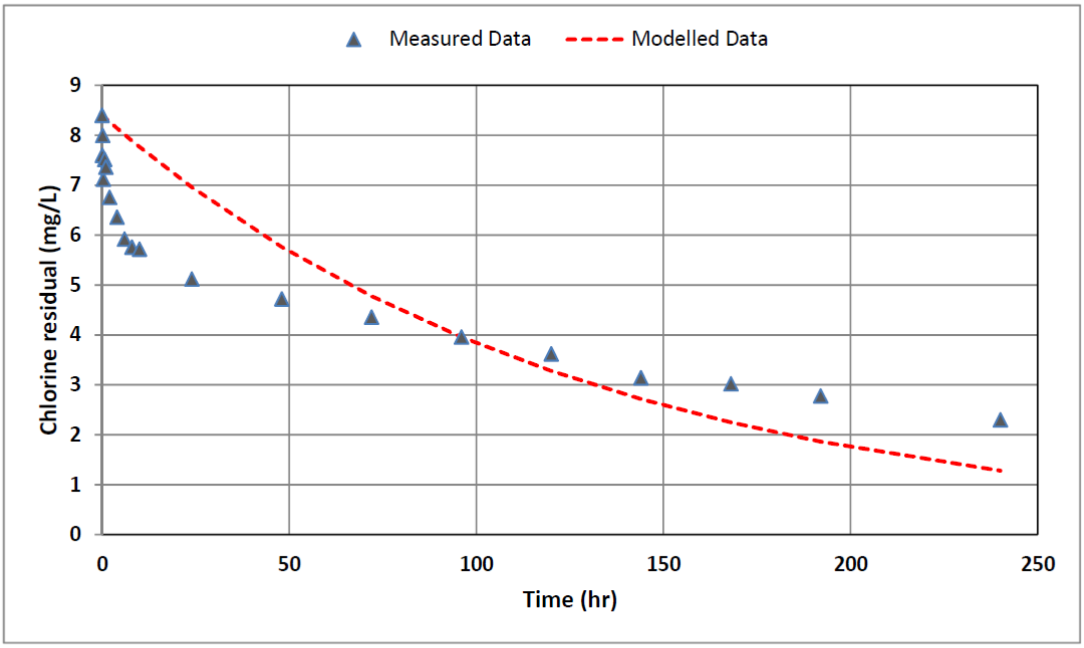


Fig.2.3. : General trend of chlorine decay behaviour vs. FOM predicted values

Although FOM is very simple to use and therefore it has always been popular, it has not provided a good data fitting for various chlorine decay data and modelling applications. In addition, the only reaction rate coefficient of FOM, k, appears to be greatly dependent on the quality of the water source and the type of treatment process. Moreover, FOM cannot reproduce the higher decay rates that are observed in the initial stages of chlorination nor the slow rates near the end of decay profiles (Jabari Kohpaei et al., 2010; Fisher et al., 2010a; Kastl et al., 1999; Clark et al., 2002).

As mentioned earlier, almost all first order kinetic models include only two variables, chlorine concentration and time. In fact, first order modelling concept either simply neglects the effects of other reacting agents or assumes their amount to be much larger than chlorine. With latter assumption, concentration of reacting agents is assumed to not change considerably during reaction with chlorine. Allowing for this assumption results in the reaction rate being only proportionate to the chlorine concentration. This leads to the so-called pseudo-first-order modelling scheme. However, the assumption would not be necessarily valid in all applications.

2.13.2.2. Parallel First Order Model (PFOM):

The parallel first order model (PFOM) was first introduced by Hass and Karra (1984). PFOM was developed based on the assumption that chlorine decay may proceed through two general parallel reactions between chlorine and two other notional reactants in water. In their model, component X (an unknown portion of free chlorine in water) with concentration C_0x, is assumed to decay according to first order kinetics with a rate constant of k_1 and the remainder, which is the initial chlorine residual without component X with concentration of $C_0(1-x)$, is subject to first order decay with a rate constant of k_2. By definition, x is limited to a range between zero and unity. Without giving further information on the detailed kinetics of the model, Hass and Karra proposed the following equation for their model:

$$C = f(C_0.t) = C_0xe^{-k_1t} + C_0(1-x)e^{-k_2t} \tag{2.33}$$

in which, $C = f(C_0.t)$ is the chlorine concentration (mg/L) at time t, C_0 is the initial concentration of the chlorine, k_1 is the fast reaction rate constant of the chlorine decay associated with C_0x and k_2 is the slow reaction rate constant of the chlorine decay associated with $C_0(1-x)$.

Gang et al. (2002) employed the same method for modelling chlorine decay and gave more specific information on deriving the model equations. They considered separating natural organic matters (NOMs) into “two distinct types of reacting agents” reacting with chlorine via two parallel reaction pathways both forming halogenated by-products. Gang et al. (2002) assumed that “one fraction of NOM, possibly associated with aldehyde and phenolic hydroxyl, was presumably involved in rapid reaction with chlorine while another fraction resulted in slow rate of chlorine consumption”. This assumption is acceptable since it is already known that many components with different reactivity with chlorine are subject to react with chlorine. Therefore, although it does not represent the exact reaction complex occurring between chlorine and all natural organic matters, those assumptions are understandable. However, the last part of their assumption, which is separating the chlorine into two fractions each reacting with different reactant does not comply with the mathematical principles of the first order model and therefore is not fundamentally valid.

PFOM was proved in many researches to achieve the best results in prediction of chlorine decay residuals. However, as mentioned above, PFOM suffers from a fundamental problem which is separating chlorine into two distinct parts whilst reacting with other substances in water. In fact, from a theoretical point of view, separating chlorine into two constituents, assuming that one part is being decayed fast whereas decay of another part is slow, does not appear to be fundamentally valid.

2.13.2.3. Second Order Model (SOM):

Considering the impact of reactant agents, Clark and Sivaganesan (1998) proposed a two-component second-order chlorine decay model based on a hypothetical reaction between chlorine and another notional substance:

$$\mathrm{aA} + \mathrm{bB} \rightarrow \mathrm{pP} \tag{2.34}$$

where A represents chlorine and B represents all individual organic and inorganic substances that could potentially react with chlorine. P represents the product of the reaction and a, b and p are the stoichiometry parameters. Clark and Sivaganesan (1998) proposed an analytical solution for this model, which appears to be the first successful analytical solution for the second-order model:

$$\mathrm{C_A} = \frac{\mathrm{K}}{1 - \mathrm{R}e^{-\mathrm{ut}}} \tag{2.35}$$

where $\mathrm{C_A}$ is the initial chlorine concentration and K, R and u are constant parameters that need to be estimated.

Due to the fact that chlorine reacts with many organic and inorganic compounds with various mechanisms and stoichiometry, having stoichiometry parameters does not appear to be appropriate. Therefore, Clark's equation can be modified using simple stoichiometry for the chlorine reaction:

$$\mathrm{Cl_2} + \mathrm{A} \overset{\mathrm{k}}{\rightarrow} \text{inert product} \tag{2.36}$$

$$\mathrm{C_{Cl}(t)} = \frac{\mathrm{C_{Cl_0}} - \mathrm{C_{A_0}}}{1 - \frac{\mathrm{C_{A_0}}}{\mathrm{C_{Cl_0}}} * e^{-(\mathrm{C_{Cl_0}} - \mathrm{C_{A_0}}) * \mathrm{k} * \mathrm{t}}} \tag{2.37}$$

where $\mathrm{C_{Cl_0}}$ and $\mathrm{C_{A_0}}$ are initial concentrations of chlorine and the notional reactant respectively and k is the rate coefficient.

Huang et al., 2007 made an attempt to prove that Clark and Sivaganesan (1998) made a mistake in correctly deriving the equation and tried to develop the correct formula for SOM. Fisher et al. (2010), however, reviewed both papers and showed that Clark and Sivaganesan (1998) was right and only made a minor typing error about a negative sign, which did not have any impact on the final result. On the other hand, Huang made a bigger mistake while deriving the integration, forgetting to apply the correct boundary conditions for the integrating.

The following are the advantages of the second order model (SOM):

- SOM has only two parameters to be estimated which is an important advantage for this model.
- SOM has an explicit solution which could simplify the parameter estimation process.
- SOM meets various boundary conditions for the time and the concentrations of the reactants.

SOM, however, suffers from some major defects:

- The analytical solution equation for SOM is only valid when $\mathrm{C_{Cl_0}} \neq \mathrm{C_{A_0}}$. When $\mathrm{C_{Cl_0}} = \mathrm{C_{A_0}}$, the analytical solution changes to the following equation:

$$\mathrm{C_{Cl}(t)} = \frac{\mathrm{C_{Cl_0}}}{1 - \mathrm{C_{Cl_0}} * \mathrm{k} * \mathrm{t}} \tag{2.38}$$

  This leads to a calculation problem when parameter estimation and data fitting is performed. The reason for the calculation error during parameter estimation and data fitting is that the general type/shape of the resultant analytical solution/function when $\mathrm{C_{Cl_0}} = \mathrm{C_{A_0}}$ (Equation 2.38) does not match the normal shape of a chlorine decay curve. Equation 2.38 is a partial fraction function with constant numerator. In fact the domain of this function (Equation 2.38) is $\left\{ \{0 \leq t \leq \infty \; and \; t \neq \frac{1}{\mathrm{C_{Cl_0}} * \mathrm{k}} \right\}$ whereas the general shape of chlorine decay is close to an exponential function with negative exponent for which the domain is $\{0 \leq t \leq \infty\}$.
- Another disadvantage for SOM is that it substitutes all chlorine reactions with only one global reaction. As a result, SOM is unable to illustrate the initial fast and the latter slow reaction rates that have been reported in most chlorine decay tests.

Trying to correct the defects of SOM, Clark and Sivaganesan (2002) extended their model (Clark and Sivaganesan (1998)) to include both fast and slow reaction types by separating chlorine into two components, each reacting with a single organic constituent separately. In fact, Clark and Sivaganesan (2002) combined concepts of SOM and PFOM and proposed a new chlorine decay model in order to rectify the shortcomings of both SOM and PFOM. The extended SOM is described below using the following reactions:

$$a_1 \mathrm{C}_A^1 + b_1 \mathrm{C}_B^1 \rightarrow p_1 \mathrm{P}^1 \tag{2.39}$$

$$a_2 \mathrm{C}_A^2 + b_2 \mathrm{C}_B^2 \rightarrow p_2 \mathrm{P}^2 \tag{2.40}$$

where C_A^1 is free chlorine residual reacting with group of fast reacting agents (C_B^1). C_A^2 is free chlorine residual reacting with group of slow reacting agents (C_B^2). P^1 and P^2 are the summations of the by-products of the two reactions; and a_1, a_2, b_1, b_2, p_1 and p_2 are stoichiometric coefficients.

The change in C_A^1 and C_A^2 with time can be calculated using the expressions below developed by Clark and Sivaganesan (1998):

$$C_A^1(\mathrm{t}) = \frac{\mathrm{C\,l}_0^1(1 - R_1)}{1 - \mathrm{R}_1 \mathrm{e}^{-(1-R_1)k_1 t}} \tag{2.41}$$

$$C_A^2(\mathrm{t}) = \frac{\mathrm{C\,l}_0^2(1 - R_2)}{1 - \mathrm{R}_2 \mathrm{e}^{-(1-R_2)k_2 t}} \tag{2.42}$$

where $\mathrm{C\,l}_0^1$ and $\mathrm{C\,l}_0^2$ are initial concentrations of C_A^1 and C_A^2. $C_A^1(\mathrm{t})$ and $C_A^2(\mathrm{t})$ are changes in concentrations of C_A^1 and C_A^2 with time t and R_1, R_2, k_1 and k_2 are parameters to be estimated.

Based on this model, the total initial chlorine concentration at time t=0 (Cl_0) can be considered as sum of $\mathrm{C\,l}_0^1$ and $\mathrm{C\,l}_0^2$:

$$Cl_0 = \mathrm{C\,l}_0^1 + \mathrm{C\,l}_0^2 \tag{2.43}$$

Assuming $= \frac{\mathrm{C\,l}_0^1}{Cl_0}$, the chlorine residual at time t can be predicted as below:

$$Cl(\mathrm{t}) = \frac{\mathrm{Cl}_0 Z(1 - R_1)}{1 - \mathrm{R}_1 \mathrm{e}^{-(1-R_1)k_1 t}} + \frac{\mathrm{Cl}_0(1 - Z)(1 - R_2)}{1 - \mathrm{R}_2 \mathrm{e}^{-(1-R_2)k_2 t}} \tag{2.44}$$

where $Cl(\mathrm{t})$ is the chlorine concentration at time t and Z, R_1, R_2, k_1 and k_2 are unknown parameters.

Although Clark and Sivaganesan (2002)'s extended second order model (extended SOM) was proved to produce more accurate predictions for chlorine residuals than SOM, the model has the same theoretical/fundamental problem from which the parallel first order model (PFOM) suffers. In fact, Clark and Sivaganesan (2002) did not give any justification for their main modelling assumption of separating chlorine into two different fractions, each one reacting with different notional agents (fast and slow reacting agents).

In addition, Clark and Sivaganesan (2002) confirmed that their extended second order model could not easily reach convergence during parameter estimation. In fact, Clark and Sivaganesan (2002) used special method to estimate their model parameters. As the explained, because there were more than one solutions for their model and the solutions depended on the initial values of the parameters, they performed the parameter estimation in three steps to reach convergence and stabilize the solution. Initially, employing SAS procedure NLIN (SAS 1990), they used residual chlorine values from the first 60 minutes of available chlorine decay test data to estimate the parameters R_1 and k_1 in Eq. (2.44). At the next step, $k_1$was fixed at its estimated value and other parameters Z, R_1, R_2 and k_2 were estimated in Eq. (2.44). Lastly, the values of the parameters Z, R_2 and k_2 were fixed to their estimated values and the remaining model parameters R_1 and k_1 were re-estimated using data from the first hour of the experiments. Due to difficulty in parameter estimation and obtaining converged solutions, 37 raw water data sets and 12 treated water data sets were used to develop the model and estimate the model parameters.

2.13.2.4.Parallel Second Order Model (PSOM)

The parallel second order model (PSOM) was initially proposed by Qually and Johnson (1983) when they modelled the chlorine decay due to its reaction with two types (fast and slow reacting) of fulvic acids.

Fisher and Kastl (1996) extended PSOM to include additional reactions between chlorine and two nitrogenous agents to enable PSOM to predict formation of nitrogenous by-products specially NDMAs. In fact, considering a relationship between formation of nitrogenous by-products (e.g. NDMA) and decay rate of combined chlorine existed, Fisher and Kastl (1996) proposed extra sets of reaction schemes in order to present this relationship. The PSOM reaction scheme proposed by Fisher and Kastl (1996) can be expressed as below:

$$\mathrm{Cl}^- + \mathrm{FRA} \rightarrow \mathrm{inert\ product} \qquad (2.45)$$

$$\mathrm{Cl^- + SRA \rightarrow inert\ product} \tag{2.46}$$

$$\mathrm{Cl^- + FRNA \rightarrow CCl + inert\ product} \tag{2.47}$$

$$\mathrm{Cl^- + SRNA \rightarrow CCl + inert\ product} \tag{2.48}$$

$$\mathrm{CCl \rightarrow inert\ product} \tag{2.49}$$

where $\mathrm{Cl^-}$ represents free chlorine in water, FRA is the Fast reacting Reducing Agents, SRA is the Slow reacting Reducing Agents and “inert product” represents inactive chlorinated by-products. FRNA is the concentration of Fast reacting Reducing Nitrogeneous Agents, SRNA is the concentration of Slow reacting Reducing Nitrogenous Agents in the water and CCl is the concentration of combined chlorine.

The second order reaction rates for different reactants and resulting free and combined chlorine decay rates of PSOM is given as follows (Fisher et al, 2010):

$$\frac{dC_j}{dt} = -k_j * C_{Cl} * C_j \quad j = 1 \text{ to } 4 \tag{2.50}$$

where C_j and k_j are concentration of the four reacting agents and their rate constants respectively.

$$\frac{dC_{Cl}}{dt} = \sum_j \frac{dC_j}{dt} \tag{2.51}$$

$$\frac{dC_{CCl}}{dt} = -k_{CCl} * C_{CCl} - \sum_j \frac{dC_j}{dt} \tag{2.52}$$

where C_{Cl} is free chlorine concentration and C_{CCl} and k_{CCl} are combined chlorine concentration and its rate constant respectively. In this form, PSOM has ten parameters: decay coefficients (k_j), initial concentrations (C_{0j}) for each of the four reducing agents and the parameters associated with combined chlorine (k_{CCl} and C_{0CCl}).

The reaction scheme for PSOM developed by Fisher and Kastl (1996) has ten parameters to be estimated thus generates more accurate decay profile than other existing models. However, it makes parameters more difficult to be interpreted and verified. In fact, complexity of this model may be an obstacle to understand the strengths and weaknesses of the model.

In response to abovementioned weakness of the original model, Kastl et al., 1999 proposed a less complicated version of PSOM by removing the reactions associated with combined chlorine from the reaction scheme. Kastl et al. (1999) proposed a parallel second order model by assuming that chlorine decays mainly due to its reaction with two notional constituents –fast and slow reducing agents in water. Their decay model only consists of two simultaneous parallel reactions with overall second order kinetics as described by equations 2.45 and 2.46.

Kastl et al. (1999) compared suitability of five nominated models for describing chlorine decay behaviour in a bulk water sample. They showed that the parallel second order model (PSOM) accurately satisfied the general requirements for modelling chlorine decay. They also confirmed that PSOM was the most accurate model to satisfy the criterion regarding invariance of coefficients in relation to initial dose (up to 4 mg/L), with the smallest weighted error. In addition, they showed that the model well represents re-chlorination. Later, Jabari Kohpaei and Sathasivan (2010) developed an analytical solution for the PSOM proposed by Kastl et al., 1999.

The analytical solution proposed by Jabari Kohpaei and Sathasivan (2010) is based on a simple format of the PSOM developed by Qually and Johnson (1983). Simple format of the Parallel Second Order Model can be described using the following reactions:

$$\mathrm{CL} + \mathrm{FRA} \xrightarrow{\mathrm{k_{FRA}}} \mathrm{P_1} \tag{2.53}$$

$$\mathrm{CL} + \mathrm{SRA} \xrightarrow{\mathrm{k_{SRA}}} \mathrm{P_2} \tag{2.54}$$

In these reactions, Cl is chlorine concentration, FRA is the Fast reacting Reducing Agents, SRA is the Slow reacting Reducing Agents and $\mathrm{P_1}$ and $\mathrm{P_2}$ represent inactive chlorinated by-products. $\mathrm{k_{FRA}}$ and $\mathrm{k_{SRA}}$ are the rate constants of the reactions.

Following Clark's formulation (1998) and according to second order kinetics for both above reactions, the following can be shown:

$$\frac{\mathrm{dC_{FRA}}}{\mathrm{dt}} = -\mathrm{k_{FRA}} * \mathrm{C_{CL}} * \mathrm{C_{FRA}} \tag{2.55}$$

$$\frac{\mathrm{dC_{SRA}}}{\mathrm{dt}} = -\mathrm{k_{SRA}} * \mathrm{C_{CL}} * \mathrm{C_{SRA}} \tag{2.56}$$

$$\frac{\mathrm{dC_{CL}}}{\mathrm{dt}} = \frac{\mathrm{dC_{FRA}}}{\mathrm{dt}} + \frac{\mathrm{dC_{SRA}}}{\mathrm{dt}} = -\mathrm{k_{FRA}} * \mathrm{C_{CL}} * \mathrm{C_{FRA}} - \mathrm{k_{SRA}} * \mathrm{C_{CL}} * \mathrm{C_{SRA}} \tag{2.57}$$

Considering $C_{Cl_0} = a$. $C_{FRA_0} = b$ and $C_{SRA_0} = c$, the following formulas have been obtained for PSOM:

$$C_{Cl_{FRA}}(t) = \frac{a - b}{1 - \frac{b}{a} e^{-(a-b)k_{FRA}t}} \tag{2.58}$$

$$C_{Cl}(t) = \frac{C_{Cl_{FRA}}(t) - c}{1 - \frac{c}{C_{Cl_{FRA}}(t)} e^{-\left(C_{Cl_{FRA}}(t) - c\right)k_{SRA}t}} \tag{2.59}$$

2.14. Summary and Conclusion

In this chapter, initially, history of chlorine disinfection and basic chlorine chemistry was briefly discussed. Then, basic requirements for effective chlorination were explained and finally history of chlorine decay modelling in water distribution systems and the most popular existing chlorine decay models were characterized.

Existing chlorine decay models in the literature were categorized into two categories: data-based (empirical) models versus process-based (theoretical or mechanistic) models. Process-based models were given more attention due to their more popularity in the literature and their capability in predicting chlorine residuals in all planning and management applications.

Amongst all existing process-based chlorine decay models in the literature, the most popular ones including first order reaction model (FOM), second order model (SOM), parallel first order (PFOM) and parallel second order model (PSOM) were paid more attention and compared more carefully.

3. Materials and Methods

This chapter describes the methods and procedures for analysing water samples and measuring water quality parameters of interest.

3.1. Collection of Water Samples

Water samples were collected from various water resources in Western Australia, including the Harding Dam Water Treatment Plant in Western Pilbara and Mundaring Weir. At each site, water samples were collected from different locations within the site in order to provide an appropriate representation of water quality for each site. Collected samples were stored in 10-20 litre cleaned plastic containers. Full containers were properly sealed and labelled to keep record of information on their sampling locations, date and time. Collected samples were then sent to Water Quality Laboratory at Civil Engineering Department in Curtin University for testing.

3.2. Water Sample Storage

After receiving the water samples, they were transferred into 5 litre chlorine-demand-free amber containers. The new containers were labelled to ensure sampling information will not be lost. The new full containers were then kept in the laboratory fridge at 4ºC temperature for future testing.

3.3. Sample Preparation

Prior to conducting water quality and chlorine decay tests for the collected samples, several preparation steps need to be followed to make the water samples ready for testing. These steps include filtering the water samples, preparing accurate volumes of the samples, duplication of samples, pH adjustment and labelling.

3.3.1. Filtering Water Samples

Filtering water samples was required when Dissolved Organic Carbon (DOC) measurement/test needed to be performed. To undertake filtering process, initially, the filtering apparatus and pump were setup. The filtering apparatus was cleaned before filtering was begun. Cleaning the apparatus should be done to remove any unwanted substances that could contaminate the samples.

To filter the water samples 0.45μm filter papers were used. Filter paper were first rinsed using 400mL of deionised water to remove any DOC which might exist in the filter paper. Filtering process can start once the apparatus is cleaned and the filter paper is rinsed thoroughly with deionised water. In order to filter the sample, the cleaned filter was inserted into the apparatus and the sample was poured into the top part of the apparatus. Initially the water starts to filter through the filter paper very slowly. In fact, gravity helps water go through the filter gradually. The process was speed up by starting the vacuum pump. The creates vacuum pressure in the bottom part of apparatus to assist filtering process performed more quickly. Starting vacuum pump was usually required for all samples. In some occasions, when the filter paper was clogged, the paper was replaced with a new filter paper and rinsed with deionised water. This process was continued until enough filtered water sample was collected.

Fig.3.1.: Filtering Apparatus and suction pump

3.3.2. Preparation of Filtered Water Samples

Before chlorine decay tests been undertaken, it is advisable to prepare the filtered water samples into manageable and accurate volumes so they can be dosed with required amount of chlorine and be measured for their decay tests. Two methods were examined for chlorine dosing of the filtered water samples.

Method 1:

In this method, fixed volume of the water samples were prepared to a certain amount first. Each sample was made to a volume of 500mL in a 600mL bottle. In order to measure the volume of the samples accurately, the samples were weighed, instead of using a measuring cylinder. The samples were then chlorinated using a small amount of condensed chlorine solution assuming that small amount of chlorine solution did not affect the total volume considerably.

Method 2:

In this method, some amount of filtered water sample was poured into a volumetric flask. A certain amount of diluted chlorine solution was then added to the sample and the total volume of the sample was made to 500mL.

The second method for chlorination of the filtered water samples was found to be more accurate during the lab experiments.

3.3.3. Duplication of Filtered Water Samples

During chlorine decay testing, errors can occur. Sometimes anomalies due to equipment or human errors can impact the results of experiments significantly. In order to avoid significant errors and reduce uncertainties during experiments duplicate samples were made for each water sample. This is to ensure consistency when measuring chlorine decay and to verify the results. By duplicating the samples, results of chlorine decay test for each sample can be compared to the duplicate sample so any anomalies can be picked up in the results. Therefore, for most of the tests two sets of 500mL sample were prepared.

3.3.4. pH Adjustment of the Water Samples

pH value is a measurement index of determination of the acidity or basicity of a solution. pH value of a water sample shows if the water is acidic, basic or neutral and also gives an estimation of how the water is acidic or basic.

It is well known that pH of water has significant impact on chlorine decay rate. Therefore, to compare the chlorine decay behaviour for different water samples, pH of the samples should be adjusted to one fixed value. Usually, the optimal pH range for chlorine decay tests is between 7.5 and 8.

pH of the water samples was measured using HACH HQ30d pH meter. If the pH was not in the desired range, to adjust the pH of the samples an acid or base was used. Sulphuric Acid solution was used as an acid and Sodium Hydroxide solution was used as a base. Concentration of both solutions was 1mol/L.

Fig.3.2.: HACH HQ30d pH monitor

It is likely that each water sample has a different initial pH value and therefore it may respond differently when acid/base is added to the sample. As a result, the pH adjustment is potentially a trial and error process. This means addition of acid/base solution to the water sample and pH measurement should continue until the desired pH value is obtained.

The initial pH of water sample was first measured using HACH HQ30d pH meter. Then, depending on the pH reading of the sample, an acid or base was added to the water sample. The sample was stirred for some time to allow the acid/base solution to change the pH. The sample was then remained still for five to ten minutes. After this time, the pH was measured again and if desired pH was not achieved yet, the process was repeated again until the intended pH range for the sample was obtained. Calcium Carbonate or Sodium Carbonate was used as buffer agents to stabilise the pH of water samples for the samples whose pH constantly fluctuated.

3.3.5. Labelling of Water Samples

After the water samples were prepared, duplicate samples were made and pH of the samples were adjusted, the water samples were labelled properly so that they were easily distinguished and not mixed up with other student's samples in the laboratory.

3.4. Water Quality Characteristics of the Samples

Water quality tests water samples taken from one source was undertaken to obtain the water quality characteristics of the source. The water quality test results provide us with information on composition of the water samples and therefore help explain the chlorine decay behaviour for each water sample.

Measurement of water quality characteristics of the water sources was undertaken before pH adjustment of the samples so the acids and bases added to the sample could not change the results. The following experiments to examine the initial water quality characteristics of the samples were undertaken:

- Total Organic Carbon (DOC)
- Dissolved Organic Carbon (TOC)
- Ammonia (NH3)
- Nitrate/Nitrite
- Total Organic Nitrogen (TON)
- Dissolved Organic Nitrogen (DON)
- pH
- UV_{254}

3.4.1. TOC/DOC Analysis

Total organic carbon (TOC) is the total amount of carbon that exists in an organic compound. TOC is often referred to a non-specific precursor for water quality. In fact, the total organic carbon (TOC) is a measurement method for the content of carbon of dissolved and undissolved organic substances in water. Dissolved organic carbon (DOC) is defined as the organic carbon that is able to pass through a filter with size generally ranged between 0.7 and 0.22 um. Therefore, DOC is the organic carbon remaining in a sample after it is filtered using a 0.45 micrometer filter paper.

General Electric Sievers 5310C Laboratory Total Organic Carbon Analyser was used to measure the total and dissolved organic carbon (Figure 3.3). To measure TOC, the water samples, were first poured into 40mL pre-cleaned glass vials. Three samples (one original and two duplicate samples) were prepared for each water source.

Before the sample was tested by the machine, it had to be flushed with deionised water to ensure the results were accurate. Then 40mL of each sample was analysed by the machine to give an average TOC and DOC reading in parts per million (ppm) or parts per billion (ppb).

Fig.3.3.: Sievers 5310C Laboratory TOC Analyser

3.4.2. Analysis of Ammonia and Nitrate/Nitrite

Analysis of ammonia, nitrate and nitrite in water samples is desirable when investigating the behaviour of combined chlorine after chlorination. Water samples from different water sources were tested for ammonia, nitrate and nitrite concentrations using AQUAKEM 200. A 2mL sample of each water source and appropriate AQUAKEM reagent are required to test the ammonia, nitrate and nitrite of water samples.

Fig.3.4.: AquaKem machine for testing Ammonia, Nitrate & Nitrite

3.4.3. TON/DON Analysis

Total Organic Nitrogen (TON) is a measure of the soluble and the particulate organic nitrogen in a water sample. TON is calculated by subtracting the Ammonia-N concentration from the TKN concentration or by subtracting the sum of the Ammonia-N, Nitrate-N and Nitrite-N concentrations from the total nitrogen (TN) concentration.

Dissolved Organic Nitrogen (DON) or Soluble Organic Nitrogen (SON) is the organic nitrogen that is measured when the sample is filtered. The analysis of TON and DON was outsourced to SGS Company, as the machinery in the Curtin University Civil Engineering Water laboratory was incapable of measuring these water quality parameters.

3.4.4. UV_{254} Measurement

UV absorbance was measured using Helios Gamma Spectrophotometer (Thermoelectron) and measured by filtering the sample through 0.45µm CA filter media. The optical design of this instrument is single beam Seya Namioka monochromator and gives only 0.05% error in measurement.

3.5. Chlorine Decay Testing

Chlorine decay measurements were performed in accordance with the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method using Lovibond pocket colorimeters.

In order to measure the total and free chlorine concentration, LOVIBOND PCcheckit Chlorine kit was used. First, around 10mL of the water sample was poured into a 10mL vial. A Free or Total LOVIBOND DPD (Diethyl-p-Phenylene Diamine) powder pillow was then added into the vial. The chemicals inside the powder pillow reacts with the chlorine in the vial and produces a pinkish colour. The vial was then shaken to stir/mix its contents and was left for two minutes. Afterwards, outside the vial was cleaned and the vial was placed into the chlorine measuring device to measure the chlorine concentration at the time the powder inside the powder pillow was added. This process was repeated using the same water sample for different times.

In order to confirm the initial chlorine concentration, several experiments with de-ionized water were performed prior to undertaking the main tests. Before starting experiments, all containers and glassware were washed with de-ionized water to make sure that no chlorine demand was present.

Duplicate measurements were conducted for each sample, and the average of the results was reported. If the difference between the two results was greater than 10%, third measurement was undertaken, and the average of all three results was reported. Also, in order to minimise the effects of water quality variations, tests were repeated and the results were compared for consistency.

3.5.1. Time intervals

In order to achieve a well-defined chlorine decay profile for a particular water sample, selection of appropriate times for measurement of chlorine concentration is crucial. Chlorine decays at its highest rate during the first five minutes. After this time period, the decay rate slows down to an average from one to five hours, and finally the rate reduces gradually as the chlorine decays. As a result, it is suggested to perform the majority of the chlorine measurements during the first eight hours, particularly within the first hour after chlorine dosing. Based on above discussion, the time intervals that were selected to measure the chlorine concentration are 5min, 10min, 20min, 40min, 1hour, 2hr, 4hr, 6hrs and 24hrs after dosing. For the water samples for which chlorine took longer than 24 hours to completely diminish, measurements were taken on a daily basis until the concentration of chlorine was less than 0.05mg/L.

3.5.2. Incubation

The water samples were incubated in water baths between chlorine concentration measurements. The samples were examined at the temperatures of 25 and 35˚C.

3.6. Disinfection By-Product Collection and Testing

In order to measure Disinfection by-Products, especially THMs and HAAs, 40mL of water samples were collected and set aside immediately after the samples were dosed with chlorine. The water samples were kept to be tested for Disinfected By-Product (DBPs) formation, more specifically for measurement of Trihalomethanes (THMs) formation.

A chlorine quenching agent was used to remove the rest of chlorine in the water sample (dechlorinate the sample) when the sampling for measurement of THM and HAA was intended in the middle of chlorine decay. Sodium Thiosulphate ($Na_2S_2O_3$) was used as quenching agent. A 1% Sodium Thiosulphate solution was prepared and used to quench the chlorine residual for all experiments.

When all stages of chlorine decay had occurred and therefore samples were ready, the 40mL samples were sent to SGS Company to measure for the THM and HAA concentrations.

3.7. Chlorine Quenching Sample Calculation

Based on reaction equation for the chemical reaction between Sodium Thiosulphate and chlorine, 316gr of $Na_2S_2O_3$ reacts with 71gr of chlorine to form Sodium Tetrationate and sodium chloride:

$$2\mathrm{Na_2S_2O_3(aq)} + \mathrm{Cl_2(aq)} \rightarrow \mathrm{Na_2S_4O_6(aq)} + 2\mathrm{NaCl(aq)} \qquad (3.1)$$

Therefore, to quench 1mg/lit of chlorine, 4.45 mg/L (~5 mg/L) of Sodium Thiosulphate is required. Therefore, if 1% Sodium Thiosulphate solution is prepared, $20\ \mu L$ of the solution is required to quench 1mg/L of chlorine in a 40mL vial.

3.8. Data Analysis:

In order to evaluate the accuracy of a modelling approach, the weighted error between experimental and model data (χ^2) can be used as a measure of goodness of fit between experimental and predicted data and can be defined as follows:

$$\chi^2(\mathrm{p}) = \sum_{\mathrm{i}=1}^{\mathrm{n}} \left(\frac{\mathrm{f}_{\mathrm{meas,i}} - \mathrm{f}_{\mathrm{i}}(\mathrm{p})}{\sigma_{\mathrm{meas,i}}}\right)^2 \qquad (3.2)$$

where $\mathrm{f}_{\mathrm{meas,i}}$ is the ith measured value, $\mathrm{f}_{\mathrm{i}}(\mathrm{p})$ is the calculated value from the model using parameter values p and $\sigma_{\mathrm{meas,i}}$ is the estimated standard deviation of $\mathrm{f}_{\mathrm{meas,i}}$.

Two methods were used to perform data analysis and parameter estimation for chlorine decay modelling of the selected data. Data analysis for chlorine decay modelling of some data sets was performed using prepopulated Excel spreadsheets and Excel Solver Add-in is used to undertake parameter estimation for those data. Also, Aquasim has been used to undertake the parameter estimation when more sophisticated data analysis methods to achieve accurate results were required.

3.8.1. Excel Solver

Excel Solver is created as part of a set of commands referred to as What-if Analysis Tools in Microsoft Excel. It is mainly designed to perform simulation and optimization for various business and engineering models. The Excel Solver add-in is specifically suitable for solving linear problems and aka linear optimization problems. However, it can also be used for solving smooth nonlinear and non-smooth problems.

The following methods/algorithms have been incorporated into the Excel Solver Add-in program:

GRG Nonlinear Algorithm:

Generalized Reduced Gradient (GRG) Nonlinear algorithm is used for problems that are smooth nonlinear, i.e. at least one of the constraints is a smooth nonlinear function of the decision variables.

LP Simplex Method:

The Simplex LP Solving method is based on the Simplex algorithm created by George Dantzig (an American mathematical scientist). It is used for solving the so-called Linear Programming problems and mathematical models in which the requirements are described by linear relationships, i.e. consist of a single objective represented by a linear equation that must be maximized or minimized.

Evolutionary Method:

This method is normally used for non-smooth problems, which are usually the most difficult type of optimization problems to solve. This is because some functions are non-smooth or even discontinuous, and therefore it's difficult to determine the direction in which a function is increasing or decreasing.

3.8.2. Aquasim:

AQUASIM contains a dynamic equation solver, which is capable of performing parameter estimation to find the best fit of the model output to the experimental data (Reichert, 1994). The fitting procedure, however, is performed based on the numerical solution of all defined reaction schemes.

During the fitting of the model to the experimental data, the initial values of all involving parameters were adjusted by AQUASIM software until χ^2 reaches a minimum value.

4. Modified Parallel First Order Model (MPFOM)

4.1. Introduction

Chlorine decay is usually described by the first order model (FOM) due to its easiness, although its weaknesses are well known. Second order model (SOM) was developed to compensate and address the issues of FOM. However, SOM is still incapable of accurately predicting chlorine residuals. In order to address the limitations of FOM and SOM, Parallel first order model (PFOM) was introduced and well described many chlorine decay profiles. However, PFOM suffers from a fundamental problem which is separating chlorine into two distinct parts, each part reacting independently with different substances in water. In this chapter, initially, this main limitation for PFOM is explained. Then, a new model is developed based on PFOM and is referred to MPFOM. Finally, MPFOM is compared with PFOM and accuracy of its results is described in details.

4.2. Parallel First Order Model (PFOM)

The parallel first order model (PFOM) was initially introduced by Hass and Karra (1984). Hass and Karra (1984) assumed that chlorine decay proceeded mainly through two reaction mechanisms, each of first order, involving a different component of the chlorine residual. In their model, part of chlorine (component X) with concentration $\mathrm{C_0x}$, is assumed to decay based on first order kinetics with a rate constant of $\mathrm{k_1}$ and the remainder, which is the initial chlorine residual without component X, $\mathrm{C_0(1-x)}$, is subject to first order decay with a rate constant of $\mathrm{k_2}$. By definition, x is limited to a range between zero and unity. Without giving further information on the detailed kinetics of the model, Hass and Karra proposed the following equation for their model:

$$\mathrm{C = f(C_0.t) = C_0xe^{-k_1t} + C_0(1-x)e^{-k_2t}} \qquad (4\cdot1)$$

in which, $\mathrm{C = f(C_0.t)}$ is the chlorine concentration (mg/L) at time t, $\mathrm{C_0}$ is the initial concentration of the chlorine, $\mathrm{k_1}$ is the rate constant of the chlorine decay associated with $\mathrm{C_0x}$ and $\mathrm{k_2}$ is the rate constant of the chlorine decay associated with $\mathrm{C_0(1-x)}$.

Gang et al. (2002) used the same method to predict chlorine decay but with a different and more specific explanation about the reacting agents. Their initial assumption was to separate natural organic matters (NOMs) into “two distinct types of reacting agents” which may react with chlorine via two parallel reactions forming halogenated by-products. Gang et al. (2002) developed their mathematical model for predicting chlorine decay based on following assumptions:

- Chlorine reacts with two distinct types of reactive NOM species via two parallel reactions which result in formation of halogenated organic by-products. One NOM functionality possibly attributes to aldehyde and phenolic hydroxyl groups and its reaction with chlorine results in a very rapid rate of chlorine consumption. The other NOM functionality is less reactive, such as activated double bonds or methyl groups, and their reaction with chlorine results in a slow, long-term chlorine demand.
- The rate of reaction for each chlorine-consuming reaction is first-order in chlorine concentration.
- Chlorine demand is solely attributed to reaction with NOM. The applied chlorine dose is selected to give a chlorine residual of approximately 1 mg/L after five days of reaction.
- In absence of inorganic demand, all chlorine consumption results in proportional formation of DBP species.

Gang et al. (2002) described their model using the following chemical reactions and relevant kinetic equations for the chlorine consumption:

$$\mathrm{NOM_R + CL_2 \overset{k_R}{\rightarrow} R - X\ (rapid)} \qquad (4 \cdot 2)$$

$$\frac{\mathrm{dC_R}}{\mathrm{dt}} = -\mathrm{k_R} * \mathrm{C} \qquad (4 \cdot 3)$$

$$\mathrm{NOM_S + CL_2 \overset{k_S}{\rightarrow} R - X\ (slow)} \qquad (4 \cdot 4)$$

$$\frac{\mathrm{dC_S}}{\mathrm{dt}} = -\mathrm{k_S} * \mathrm{C} \qquad (4 \cdot 5)$$

In this model, C is the chlorine concentration, $\mathrm{C_R}$ and $\mathrm{C_S}$ are considered to be the chlorine concentrations participating in the hypothetical separate rapid and slow reactions respectively and R-X(rapid) and R-X(slow) are chlorinated by-products. $\mathrm{k_R}$ and $\mathrm{k_S}$ are the first-order rate constants for rapid and slow reactions (h^{-1}), respectively.

Assuming that $\mathrm{C_{R0}}$ (mg/L) is the initial chlorine concentration participating in rapid reaction, $\mathrm{C_{S0}}$ is the initial chlorine concentration participating in slow reaction (mg/L),

C_0 is the initial chlorine concentration (dose) and f represents the fraction of chlorine demand attributed to rapid reaction, the following relationship between initial concentrations of various reacting elements can be considered:

$$C_{R0} = f * C_0 \qquad (4 \cdot 6)$$

Therefore:

$$C_{S0} = (1 - f) * C_0 \qquad (4 \cdot 7)$$

Using above equations and integrating the rate equations (5.3) and (5.5), Gang et al. (2002) derived the following equation for their model which was later described as the Parallel First Order Model (PFOM) for modelling chlorine decay:

$$C(t) = C_0\left\{fe^{-k_R t} + (1 - f)e^{-k_S t}\right\} \qquad (4 \cdot 8)$$

where $C(t)$ is the chlorine concentration (mg/L) at any time t.

Gang et al. (2002) used this model to predict Disinfection By-Products (THM and HAA) formation, assuming that DBP formation is a direct result of the chlorine consumption:

$$DBP(t) = D\big(C_0 - C(t)\big) \qquad (4 \cdot 9)$$

in which, DBP is the total concentration (mg/L) of THAs and HAAs and D is the overall DBP yield coefficient and is defined as the ratio of the concentration (mg/L) of DBPs formed to the concentration of chlorine consumed (mg/L).

The proposed PFOM appears to be broadly accepted and used by other researchers. Most of the researchers who have used PFOM as their preferred approach for modelling chlorine decay have confirmed that the model is one of the best methods for modelling chlorine decay in bulk water.

March et al. (2005) described the residual chlorine decay in grey water using several theoretical models including PFOM. They concluded that PFOM with four model parameters is the best model in describing chlorine decay in grey water.

Ramos et al (2009) used PFOM to assess the influence of different flow conditions in the chlorine decay of drinking water systems. An intensive study was developed based on a series of experiments tested on a loop pipe linked to the Lisbon water distribution system. Water samples and chlorine measurements were taken under three distinct flow conditions: (1) steady-state regimes; (2) combined flow situations—an initial steady-state period followed by successive transient events and a new steady-state period; (3) isolated flow test—steady-state flow regimes and transient flow regimes performed independently. Ramos et al (2009) used PFOM for their modelling procedure as they noted that the model better reproduced chlorine decay behaviour.

Vieira et al. (2004) evaluated the influence of several water quality parameters, such as temperature, initial chlorine dosage, organic matter and iron content on free chlorine bulk decay. They assessed the performance of five alternative kinetic models for describing the disinfectant behaviour, considering both static and steady-state flow conditions. Vieira et al. (2004) concluded that for the conditions tested, a parallel pseudo-first order model provided the best results.

4.3. Correction of PFOM Formulation Developed by Gang et al. (2002)

As mentioned earlier, development of PFOM has not been described well by Hass and Karra (1984). They did not provide details of derivation and calculations for development of their proposed PFOM. Gang et al. (2002), on the other hand, without providing reference to Hass and Kara (1984)'s work, proposed this model as their new modelling approach. Gang et al. (2002) provided details of how to derive PFOM’s final equation based on certain assumptions. Despite that, Gang et al. (2002)'s equations for development of PFOM contain errors. The main error is relating the decay rates for $\mathrm{C_R}$ and $\mathrm{C_S}$ to the whole chlorine concentration (C) using equations 4.3 and 4.5. Equations 4.3 and 4.5 cannot yield the final equation for PFOM (equation 4.8). Therefore, Gang et al. (2002)’s equations for development of PSOM are partially inaccurate and contain errors. In fact, equations 4.3 and 4.5 provide incorrect relationship between $\mathrm{C_R}$, $\mathrm{C_S}$ and C. The following equations show the correct forms of the PSOM formulations (compare equation 4.3 with 4.11 and equation 4.5 with 4.14):

$$\mathrm{NOM_R} + \mathrm{C_R} \overset{\mathrm{k_R}}{\rightarrow} \mathrm{R} - \mathrm{X}\ (\mathrm{rapid}) \qquad (4 \cdot 10)$$

$$\frac{\mathrm{dC_R}}{\mathrm{dt}} = -\mathrm{k_R} * \mathrm{C}_R \qquad (4 \cdot 11)$$

$$\rightarrow\ \mathrm{C}_R(\mathrm{t}) = \mathrm{C}_{R0} e^{-\mathrm{k_R} t} \qquad (4 \cdot 12)$$

$$\mathrm{NOM_S} + \mathrm{C_S} \overset{\mathrm{k_S}}{\rightarrow} \mathrm{R} - \mathrm{X}\ (\mathrm{slow}) \qquad (4 \cdot 13)$$

$$\frac{\mathrm{dC_S}}{\mathrm{dt}} = -\mathrm{k_S} * \mathrm{C}_S \qquad (4 \cdot 14)$$

$$\rightarrow \ C_S(t) = C_{S0}e^{-k_S t} \qquad (4 \cdot 15)$$

$$C(t) = C_R(t) + \ C_S(t) \qquad (4 \cdot 16)$$

$$C_0 = C_{R0} + \ C_{S0} \qquad (4 \cdot 17)$$

Assuming that $C_{R0} = fC_0$ and $C_{S0} = (1 - f)C_0$ and adding equations 4.12 and 4.15 yields equation 4.8.

4.4. The Main Issue of PFOM

Based on the parallel first order decay model, proposed by Hass and Karra (1984) and further introduced by Gang et al. (2002), chlorine is hypothetically divided into two parts, each part is assumed to decay independently according to first order kinetics with its own individual decay rate. In fact, the parallel first order model completely ignores the existence and impact of other reactants ($\mathrm{NOM_R}$ and $\mathrm{NOM_S}$). Ignoring $\mathrm{NOM_R}$ and $\mathrm{NOM_S}$ concludes that rapid and slow chlorine decay pathways may occur simultaneously with no influence from NOMs with following reaction equations:

$$\mathrm{CL_2} \overset{k_R}{\rightarrow} \mathrm{R - X}\ \text{(rapid)} \qquad (4 \cdot 18)$$

$$\mathrm{CL_2} \overset{k_S}{\rightarrow} \mathrm{R - X}\ \text{(slow)} \qquad (4 \cdot 19)$$

Form kinetics point of view, the above equations cannot occur concurrently unless chlorine is separated into two separate portions, assuming that each portion decays independently. This changes equations 4.18 and 4.19 to the following equations:

$$\mathrm{C_R} \overset{k_R}{\rightarrow} \mathrm{R - X}\ \text{(rapid)} \qquad (4 \cdot 20)$$

$$\mathrm{C_S} \overset{k_S}{\rightarrow} \mathrm{R - X}\ \text{(slow)} \qquad (4 \cdot 21)$$

However, from a theoretical viewpoint, separating chlorine into two constituents, assuming that one part is being decayed fast whilst the decay of another part is slow, does not appear to be fundamentally valid.

4.5. Modified Parallel First Order Model (MPFOM)

As mentioned earlier, the parallel first order model does not consider the effect of other reactants except chlorine in water. Considering the impact of other reactants on chlorine decay, PFOM can be modified to include the impact of other reactants. The new chlorine decay model, which is referred to the modified parallel first order model

(MPFOM), consists of two simultaneous parallel reactions with the overall second order kinetics as follows:

$$\mathrm{Cl} + \mathrm{FRA} \rightarrow \text{inert product} \tag{4·22}$$

$$\mathrm{Cl} + \mathrm{SRA} \rightarrow \text{inert product} \tag{4·23}$$

where Cl represents the chlorine species, FRA is the representative for Fast Reacting Agents and SRA is the symbol for Slow Reacting Agents in the water.

Rewriting equations 5.22 and 5.23, chlorine reactions with FRA and SRA could be shown using the following reactions:

$$\mathrm{Cl} + \mathrm{FRA} \xrightarrow{k_{FRA}} P_1 \tag{4·24}$$

$$\mathrm{Cl} + \mathrm{SRA} \xrightarrow{k_{SRA}} P_2 \tag{4·25}$$

As mentioned earlier, in the above reactions, Cl is the chlorine agent, FRA and SRA are the fast and slow reacting agents and P_1 and P_2 are the products of the reactions between chlorine and FRA and SRA, respectively. According to the first order kinetics for the above reactions:

$$\frac{dC_{\mathbf{FRA}}}{dt} = -k_{\mathbf{FRA}} * C_{\mathbf{FRA}} \tag{4·26}$$

$$\rightarrow\ C_{FRA} = C_{FRA_0} e^{-k_{\mathbf{FRA}} t} \tag{4·27}$$

$$\frac{dC_{\mathbf{SRA}}}{dt} = -k_{\mathbf{SRA}} * C_{\mathbf{SRA}} \tag{4·28}$$

$$\rightarrow\ C_{SRA} = C_{SRA_0} e^{-k_{\mathbf{SRA}} t} \tag{4·29}$$

where C_{FRA} and C_{SRA} are the concentrations of FRA and SRA in [mg/L] and k_{FRA} and k_{SRA} are the rate constants of the FRA and SRA reactions in [$h^{-1}(mg/L)^{-1}$], respectively.

As can be seen from above equations and in contrary to the original version of PFOM, in the modified version (MPFOM), the rates of the reactions between chlorine and the two hypothetical reactants (FRA and SAR) in the water are not independent of the concentrations of the reactants ($C_{\mathbf{FRA}}$ and $C_{\mathbf{SRA}}$).

According to the mass balance at time t, the amount of material subtracted from FRA and SRA is equal to that of Cl. Assuming that C_{Cl_0} represents the initial concentration of chlorine, C_{FRA_0} and C_{SRA_0} are the initial concentrations of FRA and SRA, respectively, and x and y are the concentrations of FRA and SRA that have reacted with chlorine at time t, then:

$$C_{FRA} = C_{FRA_0} - x \rightarrow \quad x = C_{FRA_0} - C_{FRA} \tag{4·30}$$

using Equation (4.27):

$$\rightarrow \quad x = C_{FRA_0} - C_{FRA_0} e^{-k_{\mathbf{FRA}}t} = \tag{4·31}$$

$$\rightarrow \quad x = C_{FRA_0}(1 - e^{-k_{\mathbf{FRA}}t}) \tag{4·32}$$

$$C_{SRA} = C_{SRA_0} - y \rightarrow \quad y = C_{SRA_0} - C_{SRA} \tag{4·33}$$

Using Equation (4.29):

$$\rightarrow \quad y = C_{SRA_0} - C_{SRA_0} e^{-k_{\mathbf{SRA}}t} = \tag{4·34}$$

$$\rightarrow \quad y = C_{SRA_0}(1 - e^{-k_{\mathbf{SRA}}t}) \tag{4·35}$$

$$C_{Cl} = C_{Cl_0} - x - y \tag{4·36}$$

$$\rightarrow \; C_{Cl} = C_{Cl_0} - C_{FRA_0}\left(1 - e^{-k_{\mathbf{FRA}}t}\right) - C_{SRA_0}\left(1 - e^{-k_{\mathbf{SRA}}t}\right) \tag{4·37}$$

where C_{Cl_0} is the initial chlorine concertation, C_{FRA_0} and C_{SRA_0} are the initial concentrations of FRA and SRA; and $k_{\mathbf{FRA}}$ and $k_{\mathbf{SRA}}$ are the rate constants for the fast and slow reactions respectively.

Equation 4.37 represents the analytical solution for the MPFOM. The following boundary conditions will be met in accordance with equation 4.37:

$$t = 0 \; \rightarrow C_{Cl} = C_{Cl_0} \tag{4·38}$$

$$t = \infty \; \rightarrow C_{Cl} = C_{Cl_0} - C_{FRA_0} - C_{SRA_0} \tag{4·39}$$

As can be seen from above equation, using MPFOM negative values for the chlorine concentrations may be estimated if the initial concentrations of other reactants exceed the initial concentration of the chlorine. This is, in fact, one of the disadvantages of MPFOM.

4.6. Assessment of MPFOM against PFOM

In this section, effectiveness of the MPFOM will be evaluated against PFOM. The criterion for evaluating the effectiveness of the models is considered to be the accuracy of the results the nominated models generate. That is how accurate the nominated models predict the chlorine residuals. The weighted error between experimental and model data (χ^2) can be used as a measure for assessment of the accuracy of the models.

4.6.1. Chlorine Decay Test Data

In order to compare the accuracy of the MPFOM with PFOM, three sets of data have been considered. These three sets of data are obtained from the free chlorine decay tests undertaken by Koechling (1998) for the water samples described in Table 4.1. Tables 4.2, 4.3 and 4.4 show the chlorine decay test data obtained by Koechling (1998) for the water samples described in Table 4.1.

Table.4.1 : Water Quality Characteristics of the Water Samples from Koechling (1998)

Sample label	**Description**	**water quality characteristics**		
		DOC (mgL^{-1})	**UVA_0 (cm^{-1})**	**Alkalinity (mg/L $CaCO_3$)**
TRW	Trinity River, TX	4.47	0.125	95
QPW	Quittacas Pond, MA	4.55	0.165	5
CLR	City Lake Reservoir, CT	2.18	0.065	21

Table.4.2 : Free Chlorine Decay Test Data for Water Sample TRW (Koechling, 1998)

Time (hrs)	**Chlorine Residual (mgL^{-1})**	**Time (hrs)**	**UAV (1/cm)**
0.0	8.90	0.0	0.12514
0.1	7.47	0.1	0.09376
0.3	6.97	0.3	0.09010
0.5	6.67	0.5	0.08957
1.1	6.35	1.1	0.08722
2.0	6.02	2.0	0.08513
4.3	5.43	4.3	0.08120
7.4	4.93	7.4	0.07977
25.3	3.74	25.0	0.07336
48.0	2.98	48.0	0.06923
74.0	2.46	74.0	0.06635
123.0	1.74	123.0	0.06375

Table.4.3 : Free Chlorine Decay Test Data for Water Sample QPW (Koechling, 1998)

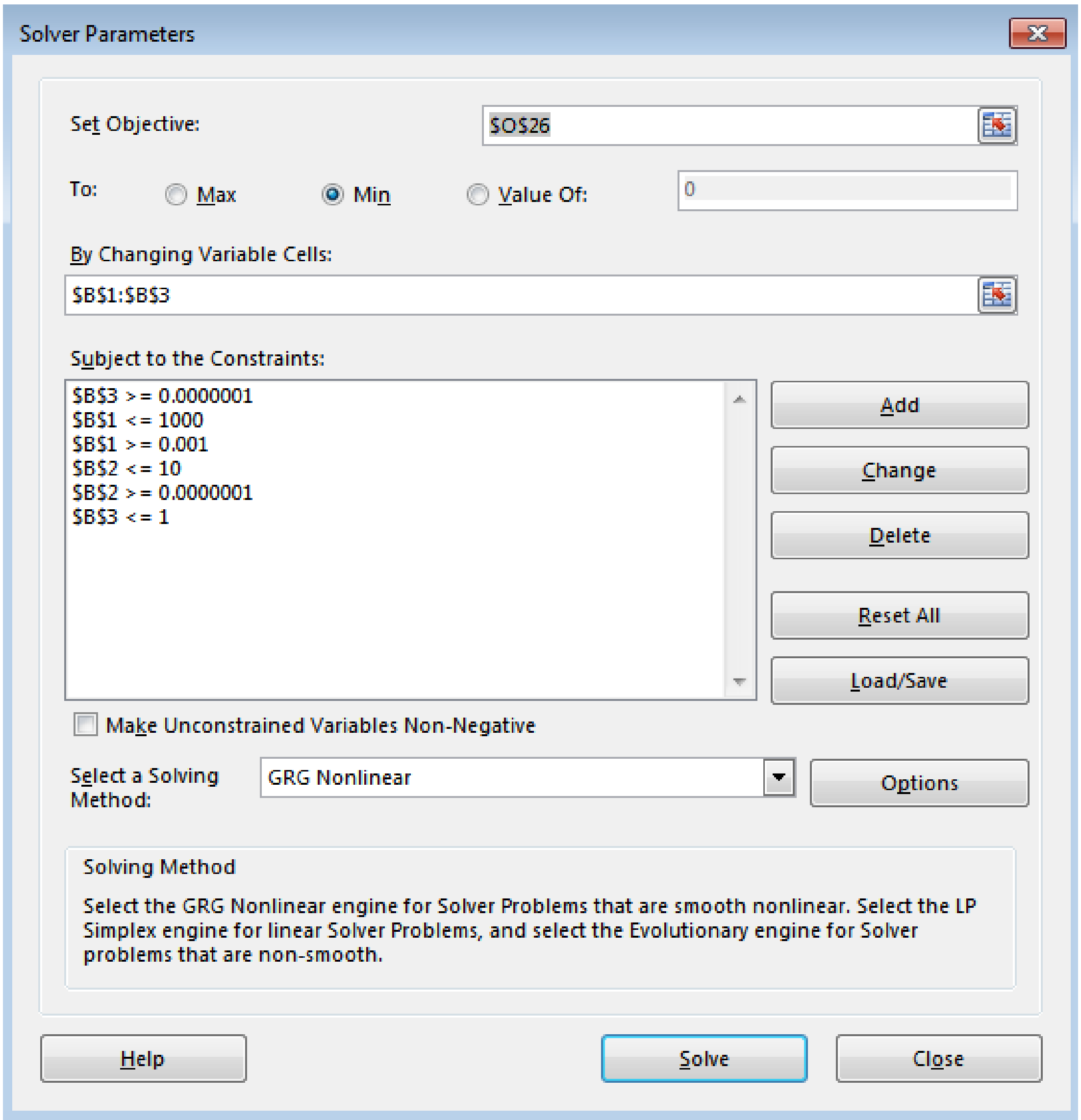
Time (hrs)	**Chlorine Residual (mgL^{-1})**	**Time (hrs)**	**UAV (1/cm)**
0.0	9.12	0.0	0.16535
0.1	7.80	0.1	0.12355
0.3	7.11	0.4	0.11762
0.5	6.63	0.5	0.11381
1.0	6.29	1.0	0.10940
2.0	5.76	2.0	0.10620
4.0	5.24	4.0	0.10144
8.0	4.57	8.0	0.09825
24.0	3.36	24.2	0.09081
48.0	2.41	48.0	0.08587
72.0	2.00	72.0	0.08237
120.0	1.17	120.0	0.07873

Table.4.4 : Free Chlorine Decay Test Data for Water Sample CLR (Koechling, 1998)

Time (hrs)	Chlorine Residual (mgL^{-1})	Time (hrs)	UAV (1/cm)
0.0	2.30	0.0	0.02574
0.1	2.04	0.1	0.01852
0.3	1.94	0.3	0.01670
0.6	1.81	0.6	0.01705
1.1	1.81	1.1	0.01616
2.1	1.71	2.1	0.01535
4.3	1.78	4.3	0.01720
8.0	1.53	8.1	0.01640
24.0	1.32	24.3	0.01280
48.0	1.09	48.0	0.01306
72.0	0.93	72.0	0.01333
120.0	0.77	120.0	0.01217

4.6.2. Data Analysis

Data analysis for chlorine decay modelling of the selected data have been performed using prepopulated Excel spreadsheets. Solver Add-in is used to undertake parameter estimation for the two nominated modelling approaches (PFOM and MPFOM). Figure 4.1 shows the Excel Solver Parameters Dialog Box.



Set Objective: $O$26

To: ○ Max ● Min ○ Value Of: 0

By Changing Variable Cells:
$B$1:$B$3

Subject to the Constraints:
$B$3 >= 0.0000001
$B$1 <= 1000
$B$1 >= 0.001
$B$2 <= 10
$B$2 >= 0.0000001
$B$3 <= 1

☐ Make Unconstrained Variables Non-Negative

Select a Solving Method: GRG Nonlinear

Solving Method

Select the GRG Nonlinear engine for Solver Problems that are smooth nonlinear. Select the LP Simplex engine for linear Solver Problems, and select the Evolutionary engine for Solver problems that are non-smooth.

Fig.4.1.: Excel Solver Parameters Dialog Box

For both models (PFOM and MPFOM), the chlorine residuals have been predicted for each data set over the entire retention time with maximum one hour intervals. The sum of squared errors (SSE) between actual and predicted data has been calculated for each data set for both models. The SSEs, which are calculated for each data set, have then been compared between PFOM and MPFOM to evaluate the models accuracy.

4.6.3. Results and Discussions

Table 4.5 compares the results of chlorine decay modelling and parameter estimation between MPFOM and PFOM for the water sample TRW from Koechling (1998)'s study. As can be seen from the results, the results predicted by MPFOM is closer to the measured data compared to the results from PFOM. Sum Squared Error (SSE) for the predicted results from MPFOM is 0.63 compared to SSE of 1.49 for the PFOM prediction for the same data. Similarly, Tables 4.6 and 4.7 provide comparison of the chlorine decay modelling results using MPFOM and PFOM for the water samples QPW and CLR from Koechling (1998)'s study. SSE values for MPFOM for the water samples QPW and CLR are calculated to be 0.59 and 0.02, respectively. Whereas, SSE values for PFOM for the QPW and CLR water samples are estimated to be 2.86 and 0.16, respectively. Moreover, R squared (R^2) values for the results predicted using MPFOM are higher than the ones obtained using PFOM. Also, as can be seen from Figures 4.2 to 4.4, MPFOM generally produces better data fitting compared to PFOM. Therefore, it can be concluded that overall accuracy of the MPFOM is greater than PFOM. However, it should be noted that this improvement in the accuracy of the modelling results of MPFOM compared to PFOM could be due to the higher number of parameters of the MPFOM. Nevertheless, as discussed earlier, although MPFOM has higher number of parameters than PFOM that need to be estimated, it does not suffer from the fundamental issue of separating chlorine into two components, each reacting with a different reacting agent and different reaction rate.

Table.4.5 : Comparison of Chlorine Decay Modelling Results using MPFOM and PFOM for TRW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MPFOM		PFOM	
Data Set Name:		TRW (RAW) Water Sample; Koechling (1998)			
Model Parameters		FRA0	2.611	k_FRA	3.302
		SRA0	4.353	k_SRA	0.013
		k_FRA	5.165	f	0.342
		k_SRA	0.035		
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	8.90	8.90	0.00	8.90	0.00
0.10	7.47	7.83	0.13	8.04	0.32
0.30	6.97	6.80	0.03	6.97	0.00
0.50	6.67	6.41	0.07	6.41	0.07
1.10	6.35	6.13	0.05	5.86	0.24
2.00	6.02	6.00	0.00	5.72	0.09
4.30	5.43	5.68	0.06	5.55	0.01
7.40	4.93	5.30	0.14	5.34	0.17
25.30	3.74	3.74	0.00	4.26	0.27
48.00	2.98	2.76	0.05	3.20	0.05
74.00	2.46	2.27	0.04	2.31	0.02
123.00	1.74	2.00	0.07	1.24	0.25
		Sum Squared Error (SSE)	0.63	Sum Squared Error (SSE)	1.49
		R Squared (R2)	0.9882	R Squared (R2)	0.9736

Table.4.6 : Comparison of Chlorine Decay Modelling Results using MPFOM and PFOM for QPW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MPFOM		PFOM	
Data Set Name:		QPW (RAW) Water Sample; Koechling (1998)			
Model Parameters		FRA0	3.087	k_FRA	0.013
		SRA0	4.667	k_SRA	1.000
		k_FRA	3.513	f	0.540
		k_SRA	0.035		
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	9.12	9.12	0.00	9.12	0.00
0.10	7.80	8.19	0.15	8.71	0.84
0.30	7.11	7.06	0.00	8.01	0.82
0.50	6.63	6.49	0.02	7.44	0.65
1.00	6.29	5.97	0.11	6.40	0.01
2.00	5.76	5.72	0.00	5.37	0.16
4.00	5.24	5.43	0.03	4.75	0.24
8.00	4.57	4.90	0.11	4.43	0.02
24.00	3.36	3.39	0.00	3.59	0.05
48.00	2.41	2.24	0.03	2.62	0.04
72.00	2.00	1.75	0.06	1.91	0.01
120.00	1.17	1.44	0.07	1.01	0.03
		Sum Squared Error (SSE)	0.59	Sum Squared Error (SSE)	2.86
		R Squared (R2)	0.9915	R Squared (R2)	0.9734

Table.4.7 :Comparison of Chlorine Decay Modelling Results using MPFOM and PFOM for CLR Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MPFOM		PFOM	
Data Set Name:		CLR (RAW) Water Sample; Koechling (1998)			
Model Parameters		FRA0	0.489	k_FRA	0.007
		SRA0	1.079	k_SRA	1.000
		k_FRA	5.657	f	0.702
		k_SRA	0.025		
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	2.30	2.30	0.00	2.30	0.00
0.10	2.04	2.09	0.00	2.23	0.04
0.30	1.94	1.89	0.00	2.12	0.03
0.60	1.81	1.81	0.00	1.98	0.03
1.10	1.81	1.78	0.00	1.83	0.00
2.10	1.71	1.76	0.00	1.68	0.00
4.30	1.78	1.70	0.01	1.58	0.04
8.00	1.53	1.62	0.01	1.53	0.00
24.00	1.32	1.33	0.00	1.36	0.00
48.00	1.09	1.06	0.00	1.15	0.00
72.00	0.93	0.92	0.00	0.97	0.00
120.00	0.77	0.79	0.00	0.69	0.01
		Sum Squared Error (SSE)	0.02	Sum Squared Error (SSE)	0.16
		R Squared (R2)	0.9908	R Squared (R2)	0.9527

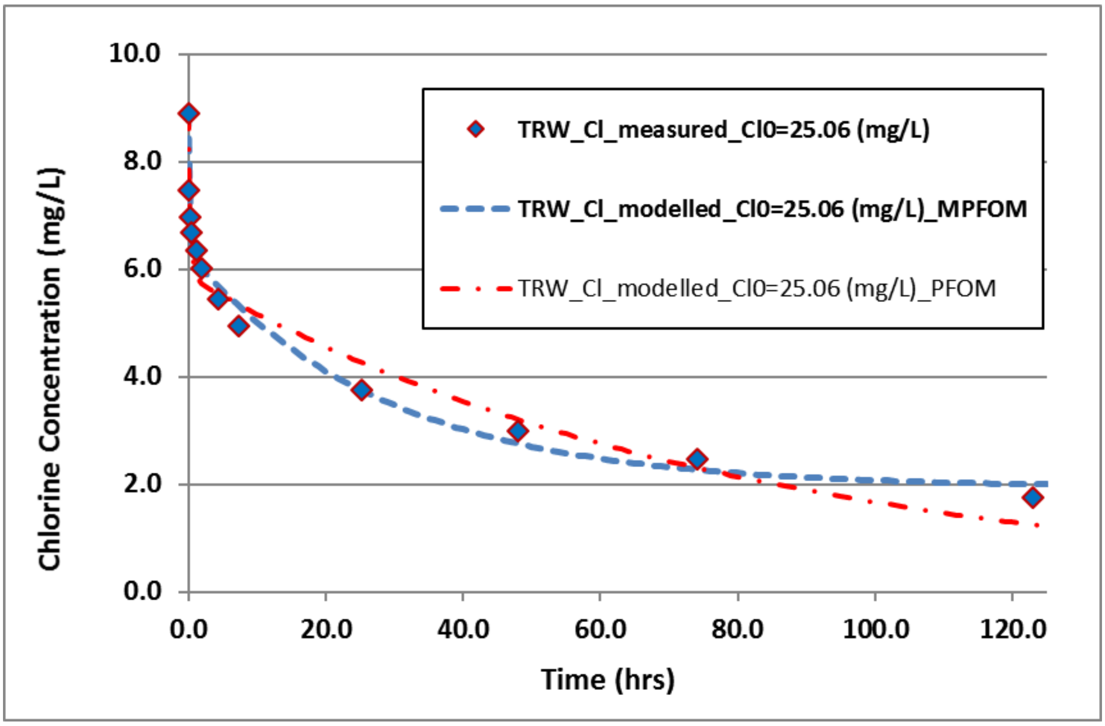


Fig.4.2.: Goodness of data fitting of chlorine decay modelling using MPFOM and PFOM for water sample TRW from Koechling (1998)'s study

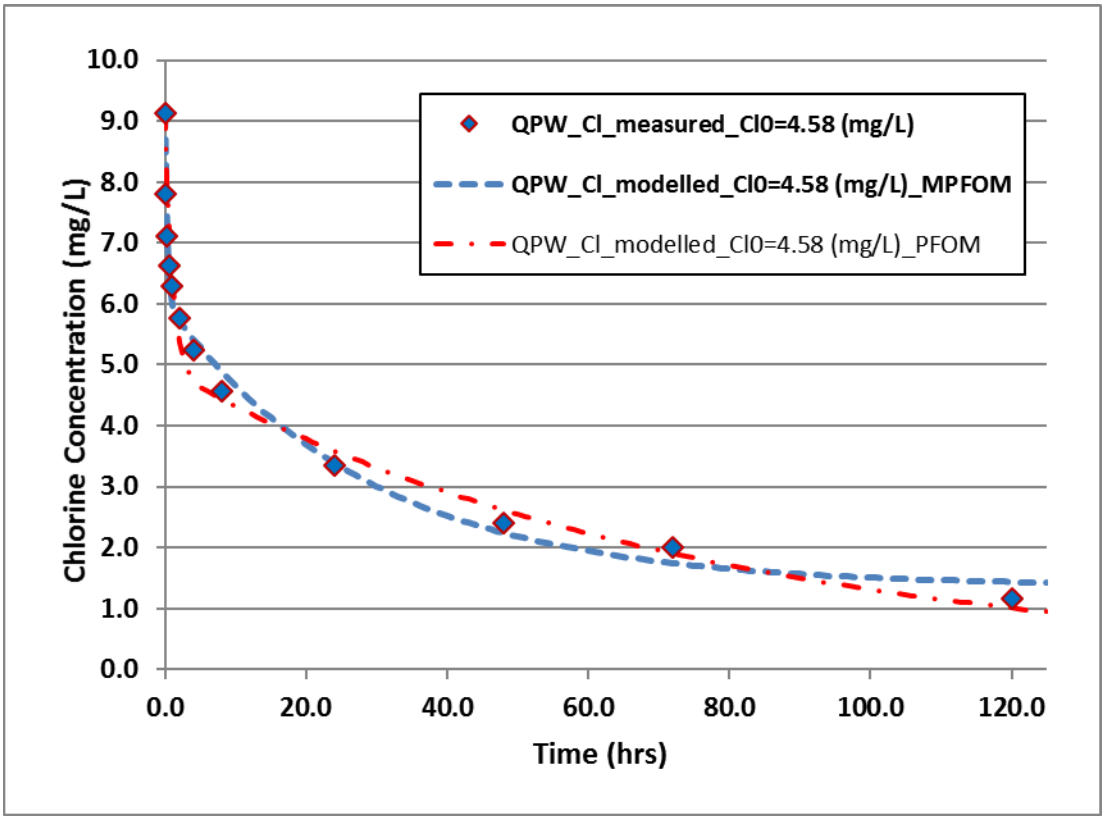


Fig.4.3.: Goodness of data fitting of chlorine decay modelling using MPFOM and PFOM for water sample QPW from Koechling (1998)'s study

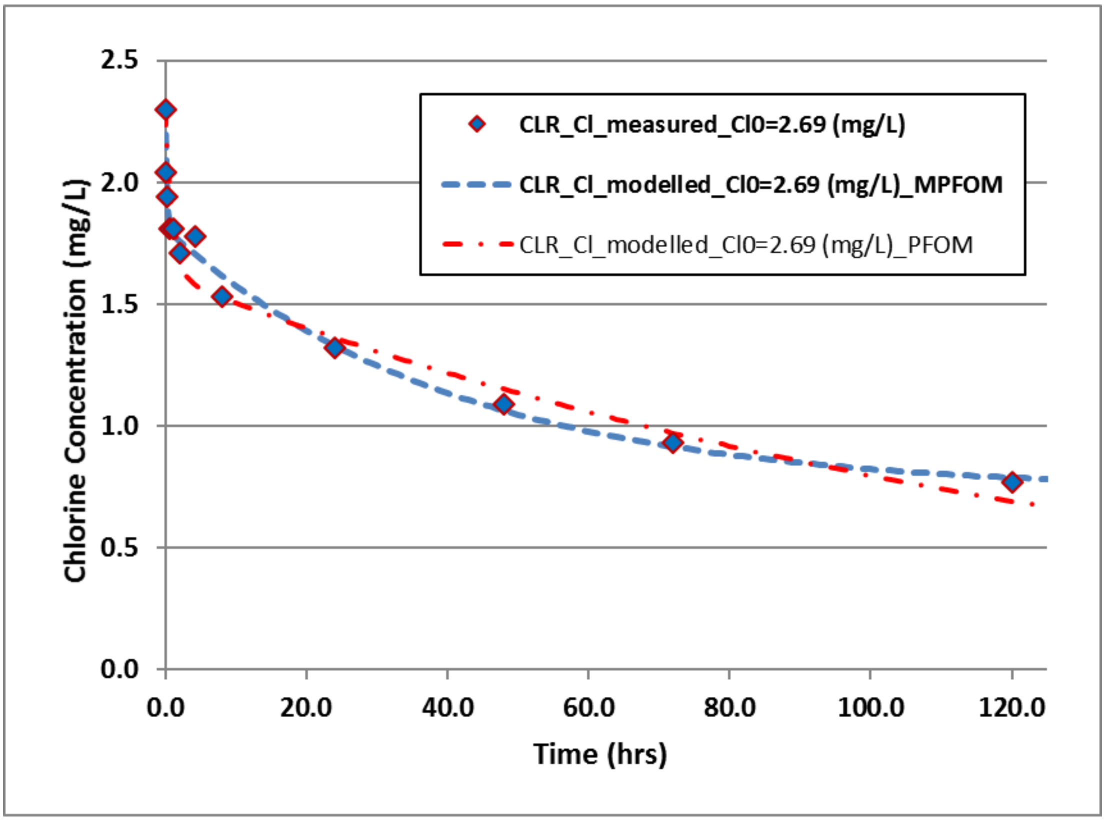


Fig.4.4.: Goodness of data fitting of chlorine decay modelling using MPFOM and PFOM for water sample CLR from Koechling (1998)'s study

4.7. Conclusion

FOM is found to be the simplest and easy to use process-based chlorine decay model. However, it is also well-known as the least accurate modelling approaches. Second order model (SOM) was developed to compensate and address the issues of FOM. However, SOM is still incapable of accurately predicting chlorine residuals. In order to address the limitations of FOM and SOM, Parallel first order model (PFOM) was introduced and well described many chlorine decay profiles. But, PFOM also has a fundamental problem which is separating chlorine into two distinct parts, each part reacting independently with different substances in water. In this chapter, a new model called modified parallel first order model (MPFOM) was developed by the author based on PFOM. Finally, MPFOM was compared with PFOM and its results were found more accurate than PFOM.

5. Modified Second Order Model (MSOM)

5.1. Introduction

One of the most well-known process based chlorine decay models is the second order model (SOM). SOM was proposed by Clark and Sivaganesan (1998) to remove the main FOM drawback, which is ignoring the impact of reactant agents. Although SOM was considered to be much superior than FOM in more accurately predicting the chlorine residuals, its prediction accuracy was still not found adequate for most of applications. The main issue of the SOM is that it substitutes all chlorine reactions with only one global reaction. As a result, SOM is unable to illustrate the initial fast and the latter slow reaction rates that have been reported in most chlorine decay tests.

In an attempt to rectify the issues of SOM, Clark and Sivaganesan (2002) extended their SOM to include both fast and slow reaction types by separating chlorine into two components, each reacting with a single organic constituent separately. In fact, Clark and Sivaganesan (2002) combined concepts of SOM and PFOM and proposed a new chlorine decay model in order to rectify the shortcomings of both SOM and PFOM. The new model contains five parameters that need to be estimated. Since their extended model had three parameters more than SOM, the model produced more accurate results for prediction of chlorine residuals. However, Clark and Sivaganesan (2002) found that the final values of the parameters of their model were very sensitive to their initial values. Therefore, it was very difficult to reach convergence during parameter estimation of their model. This issue was mentioned in Clark and Sivaganesan (2002)'s own publication. Clark and Sivaganesan (2002) had to employ a unique and complicated parameter estimation process in order to estimate the model parameters with sufficient accuracy.

In order to compare Clark and Sivaganesan (2002)'s model with other chorine decay models, the author attempted to undertake parameter estimation for their modelling approach using simple Excel Solver Add but convergence of the solution could not be obtained. However, by changing the initial values of the model parameters, in one attempt out of ten, a solution may be found. It appears that the solution is highly dependent on the initial values of model parameters.

In this chapter, first the issue of Clark and Sivaganesan (2002)'s model is explored in more details and then a new model, called modified second order model (MSOM), will be proposed to remove the drawback of the Clark and Sivaganesan (2002)'s model. Finally, MSOM will be compared with other models and its limitations are described in more details.

5.2. Development of the Second Order Model (SOM) Formula

In order to improve the accuracy of the results of the first order model (FOM), Clark and Sivaganesan (1998) introduced a two-component second-order chlorine decay model which is based on the concept of reaction between two notional substances on the assumption that the balanced reaction equation can be represented by:

$$aA + bB \rightarrow pP \qquad (5.1)$$

Clark and Sivaganesan (1998) developed an analytical solution for their model which appears to be the first successful attempt for development of an analytical solution for the second-order model (SOM). Later on, Huang et al., 2007, tried to prove that Clark and Sivaganesan (1998) were wrong in deriving the equation correctly and attempted to extract the correct formula for SOM. However, after reviewing both papers, it has been revealed that Clark and Sivaganesan (1998) were right and they just made a minor type-missing about a negative sign which did not have any impact on the final result. On the other hand, Huang et al., 2007 forgot to consider boundary conditions while integrating in order to re-derive the analytical solution for the SOM.

In equation 5.1, A and B are reacting substances, in which A represents chlorine, B represents the reacting agent and P is the product of the reaction.

The rate of the reaction can be given by:

$$\frac{dC_A}{dt} = -k_A C_A C_B \ \ or \ \frac{dC_B}{dt} = -k_B C_A C_B \ or \ \frac{dC_P}{dt} = -k_P C_A C_B \qquad (5.2)$$

where C_A , C_B and C_P are the concentrations of A, B and P at time t, respectively. k_A, k_B, and k_P are the reaction rate coefficients of A, B and P, respectively.

Based on the principle of mass balance, the following relationship can be established:

$$^{k_A}/_{a} = {}^{k_B}/_{b} = {}^{k_P}/_{p} \qquad (5.3)$$

Assuming that C_{A_0} and C_{B_0} are the initial concentrations of A and B, respectively, i.e. at t=0, and x represents the concentration of A that has reacted at time t, then the concentration of B that has reacted at time t is given by $\frac{b}{a}x$. Consequently:

$$C_A = C_{A_0} - x \tag{5.4}$$

$$C_B = C_{B_0} - \frac{b}{a}x \tag{5.5}$$

$$dC_A = -dx = \frac{a}{b}dC_B \tag{5.6}$$

Substitution 5.4 and 5.5 into 5.2 produces:

$$\frac{dC_A}{dt} = -k_A\left(C_{A_0} - x\right)\left(C_{B_0} - \frac{b}{a}x\right) \tag{5.7}$$

Substituting 5.6 into 5.7 yields:

$$\frac{dx}{\left(C_{A_0} - x\right)\left(C_{B_0} - \frac{b}{a}x\right)} = k_A dt \tag{5.8}$$

This is where Clark and Sivaganesan (1998) missed a negative sign but it was just a miss-typing error. Rearranging 5.8 yields:

$$\frac{\frac{a}{b}dx}{\left(x - C_{A_0}\right)\left(x - \frac{a}{b}C_{B_0}\right)} = k_A dt \tag{5.9}$$

Let:

$$\frac{\frac{a}{b}dx}{\left(x - C_{A_0}\right)\left(x - \frac{a}{b}C_{B_0}\right)} = \left(\frac{\alpha}{\left(x - C_{A_0}\right)} + \frac{\beta}{\left(x - \frac{a}{b}C_{B_0}\right)}\right)dx \tag{5.10}$$

Solving 5.10 gives:

$$\begin{cases} \alpha = \dfrac{1}{\frac{b}{a}C_{A_0} - C_{B_0}} \\ \beta = \dfrac{-1}{\frac{b}{a}C_{A_0} - C_{B_0}} \end{cases}$$

Substituting α and β into 5.10 yields:

$$\frac{\frac{a}{b}dx}{\left(x - C_{A_0}\right)\left(x - \frac{a}{b}C_{B_0}\right)} = \frac{1}{\frac{b}{a}C_{A_0} - C_{B_0}}\left(\frac{1}{\left(x - C_{A_0}\right)} - \frac{1}{\left(x - \frac{a}{b}C_{B_0}\right)}\right)dx \tag{5.11}$$

Substituting 5.11 into 5.9 and rearranging:

$$\left(\frac{1}{\left(x-C_{A_0}\right)}-\frac{1}{\left(x-\frac{a}{b}C_{B_0}\right)}\right)dx=\left(\frac{b}{a}C_{A_0}-C_{B_0}\right)k_A dt \qquad (5.12)$$

Defining $r=\left(\frac{b}{a}C_{A_0}-C_{B_0}\right)$ and $u=rk_A$ gives:

$$\left(\frac{1}{\left(x-C_{A_0}\right)}-\frac{1}{\left(x-\frac{a}{b}C_{B_0}\right)}\right)dx=udt \qquad (5.13)$$

Integrating 5.13 and considering the boundary conditions, which is what Huang et al. (2007) forgot, yields:

$$\ln\frac{x-C_{A_0}}{x-\frac{a}{b}C_{B_0}}+\ C=ut \qquad (5.14)$$

where C is a constant to be calculated. Using the previous definition for x, it is known that at the time t=0, x=0 then from 5.14 it can be concluded that:

$$\ln\frac{-C_{A_0}}{-\frac{a}{b}C_{B_0}}+\ C=0 \qquad \rightarrow \qquad C=-\ln\frac{bC_{A_0}}{aC_{B_0}}=\ln\frac{aC_{B_0}}{bC_{A_0}}$$

Substituting calculated C into 5.14 and rearranging yields:

$$\ln\left(\frac{x-C_{A_0}}{x-\frac{a}{b}C_{B_0}}\right)\left(\frac{aC_{B_0}}{bC_{A_0}}\right)=ut \qquad (5.15)$$

Thus

$$\left(\frac{x-C_{A_0}}{x-\frac{a}{b}C_{B_0}}\right)\left(\frac{aC_{B_0}}{bC_{A_0}}\right)=e^{ut} \qquad (5.16)$$

Then

$$\frac{x-C_{A_0}}{x-\frac{a}{b}C_{B_0}}=\frac{bC_{A_0}}{aC_{B_0}}e^{ut} \qquad (5.17)$$

$$\frac{x-C_{A_0}}{x-\frac{a}{b}C_{B_0}}=\frac{1}{\frac{aC_{B_0}}{bC_{A_0}}e^{-ut}} \qquad (5.18)$$

$$\frac{C_{A_0}-x}{\frac{a}{b}C_{B_0}-x}=\frac{1}{\frac{aC_{B_0}}{bC_{A_0}}e^{-ut}} \qquad (5.19)$$

From here, one approach is to find x and then calculate the value of C_A from equation 5.4. This, however, is a difficult method. Another method, which is easier, is to use simple mathematical equality of the fractions to get rid of x in the denominator of the left fraction in the above equation. ($\frac{a}{b} = \frac{c}{d} \rightarrow \frac{a}{b \pm a} = \frac{c}{d \pm c}$):

$$\frac{C_{A_0} - x}{\frac{a}{b} C_{B_0} - x - (C_{A_0} - x)} = \frac{1}{\frac{aC_{B_0}}{bC_{A_0}} e^{-ut} - 1} \tag{5.20}$$

$$\frac{C_{A_0} - x}{\frac{a}{b} C_{B_0} - C_{A_0}} = \frac{1}{\frac{aC_{B_0}}{bC_{A_0}} e^{-ut} - 1} \tag{5.21}$$

From (5.4):

$$\frac{C_A}{\frac{a}{b} C_{B_0} - C_{A_0}} = \frac{1}{\frac{aC_{B_0}}{bC_{A_0}} e^{-ut} - 1} \tag{5.22}$$

Then:

$$C_A = \frac{C_{A_0} - \frac{a}{b} C_{B_0}}{1 - \frac{aC_{B_0}}{bC_{A_0}} e^{-ut}} \tag{5.23}$$

Assuming $R = \frac{aC_{B_0}}{bC_{A_0}}$ and $K = C_{A_0} - \frac{a}{b} C_{B_0}$ Then:

$$C_A = \frac{K}{1 - Re^{-ut}} \tag{5.24}$$

Equation 5.24 is the same equation that Clark and Sivaganesan (1998) derived. In contrast, Huang et al. (2007) derived the following equation for SOM model:

$$C_A = \frac{K}{1 - e^{-ut}} \tag{5.25}$$

Ignoring the stoichiometry coefficients in equation 5.1 (a=b=1), and knowing that $u = rk_A = \left(C_{A_0} - C_{B_0}\right) k_A$, equation 5.23 yields to:

$$C_A = \frac{C_{A_0} - C_{B_0}}{1 - \frac{C_{B_0}}{C_{A_0}} e^{-(C_{A_0} - C_{B_0}) k_A t}} \tag{5.26}$$

By only checking the boundary conditions of both Clark and Sivaganesan (1998) and Huang et al. (2007)'s equations, it can be simply proved that Huang et al. (2007)'s formulation is wrong.

In Clark and Sivaganesan (1998)'s equation (equation 5.24), at time t=0, it yields $C_A(\mathrm{t}=0)=C_{A_0}$. However, Huang et al. (2007)'s equation gives $C_A(\mathrm{t}=0)\rightarrow\infty$ which is not correct.

5.3. Extended Second Order Model

Whilst SOM was found to produce more accurate chlorine decay results compared to FOM, its accuracy was still not considered adequate for many applications. The main reason for SOM lacking to produce accurate results was found its inability to generate the initial fast decay rate followed by the slower rate profile. Clark and Sivaganesan (2002) attempted to improve the accuracy of SOM by extending their model (Clark and Sivaganesan, 1998) to include both fast and slow reaction types by separating chlorine into two components, each reacting with a single organic constituent separately. In fact, they combined the concepts of SOM and PFOM and proposed a new chlorine decay model in order to rectify the shortcomings of both SOM and PFOM.

Based on extended version of SOM, chlorine is divided into two separate components, C_A^1 and C_A^2, and each of the two chlorine components decays separately in accordance with second order kinetics. The extended SOM can be described below using the following reactions:

$$a_1\mathrm{C}_A^1+b_1\mathrm{C}_B^1\rightarrow p_1\mathrm{P}^1 \tag{5.27}$$

$$a_2\mathrm{C}_A^2+b_2\mathrm{C}_B^2\rightarrow p_2\mathrm{P}^2 \tag{5.28}$$

where C_A^1 is free chlorine residual reacting with group of fast reacting agents (C_B^1). C_A^2 is free chlorine residual reacting with group of slow reacting agents (C_B^2). P^1 and P^2 are the summations of the by-products of the two reactions; and a_1, a_2, b_1, b_2, p_1 and p_2 are stoichiometric coefficients.

Based on this model, the total initial chlorine concentration at time t=0 (Cl_0) is considered the sum of $\mathrm{C\,l}_0^1$ and $\mathrm{C\,l}_0^2$:

$$Cl_0=\mathrm{C\,l}_0^1+\mathrm{C\,l}_0^2 \tag{5.29}$$

And the change in C_A^1 and C_A^2 with time is calculated using the formulas developed by Clark and Sivaganesan (1998):

$$C_A^1(\mathrm{t}) = \frac{\mathrm{C\,l}_0^1(1-R_1)}{1-\mathrm{R}_1\mathrm{e}^{-(1-R_1)k_1 t}} \tag{5.30}$$

$$C_A^2(\mathrm{t}) = \frac{\mathrm{C\,l}_0^2(1-R_2)}{1-\mathrm{R}_2\mathrm{e}^{-(1-R_2)k_2 t}} \tag{5.31}$$

where $\mathrm{C\,l}_0^1$ and $\mathrm{C\,l}_0^2$ are initial concentrations of C_A^1 and C_A^2. $C_A^1(\mathrm{t})$ and $C_A^2(\mathrm{t})$ are changes in concentrations of C_A^1 and C_A^2 with time t and R_1, R_2, k_1 and k_2 are parameters to be estimated.

Assuming $= \frac{\mathrm{C\,l}_0^1}{Cl_0}$, the chlorine residual at time t can be predicted as below:

$$Cl(\mathrm{t}) = \frac{\mathrm{Cl}_0 Z(1-R_1)}{1-\mathrm{R}_1\mathrm{e}\,-^{(1-R_1)k_1 t}} + \frac{\mathrm{Cl}_0(1-Z)(1-R_2)}{1-\mathrm{R}_2\mathrm{e}^{-(1-R_2)k_2 t}} \tag{5.32}$$

where $Cl(\mathrm{t})$ is the chlorine concentration at time t and Z, R_1, R_2, k_1 and k_2 are unknown parameters.

Although (Clark and Sivaganesan, 2002)'s extended second order model (extended SOM) was proved to produce more accurate predictions for chlorine residuals than SOM, the model has the same theoretical/fundamental problem from which the parallel first order model (PFOM) suffers. In fact, Clark and Sivaganesan (2002) did not give any justification for their main modelling assumption of separating chlorine into two different fractions, each one reacting with different notional agents (fast and slow reacting agents).

In addition, (Clark and Sivaganesan, 2002) confirmed that their extended second order model could not easily reach convergence during parameter estimation. In fact, (Clark and Sivaganesan, 2002) used special method to estimate their model parameters. As they explained, because there were more than one solutions for their model and the solutions depended on the initial values of the parameters, they performed the parameter estimation in three steps to reach convergence and stabilize the solution. Initially, employing SAS procedure NLIN (SAS 1990), they used residual chlorine values from the first 60 minutes of available chlorine decay test data to estimate the parameters R_1 and k_1 in Eq. (2.27). At the next step, $k_1$was fixed at its estimated value and other parameters Z, R_1, R_2 and k_2 were estimated in Eq. (2.27). Lastly, the values of the parameters Z, R_2 and k_2 were fixed to their estimated values and the remaining model parameters R_1 and k_1 were re-estimated using data from the first hour of the experiments. Due to difficulty in parameter estimation and obtaining converged solutions, 37 raw water data sets and 12 treated water data sets were used to develop the model and estimate the model parameters.

5.4. Main Issue of the Extended SOM

Reviewing how original and extended versions of the second order model (SOM) were developed, the author realized that replacement of some original parameters with new ones during development of the SOM may have caused the parameter estimation convergence issues for extended version of the SOM.

As explained earlier, (Clark and Sivaganesan, 1998) substituted some parameters for development of the SOM analytical solution as below (stoichiometry coefficients are ignored i.e. a=b=1):

$$u = \left(C_{A_0} - C_{B_0}\right)k_A \tag{5.33}$$

$$R = \frac{C_{B_0}}{C_{A_0}} \tag{5.34}$$

$$K = C_{A_0} - C_{B_0} \tag{5.35}$$

The original SOM analytical solution without the above substitutions is:

$$C_A = \frac{C_{A_0} - C_{B_0}}{1 - \frac{C_{B_0}}{C_{A_0}} e^{-(C_{A_0} - C_{B_0})k_A t}} \tag{5.36}$$

And the analytical solution formula using the substituted variables is:

$$C_A = \frac{K}{1 - Re^{-ut}} \tag{5.37}$$

As it can be noticed, some variables in the above substitution formulas (5.33 to 5.35) are interdependent. For instance, variable u which is defined as $\left(C_{A_0} - C_{B_0}\right)k_A$ can be shown as Kk_A. This dependence is not reflected in equation 5.37.

Furthermore, using substitution formulas (5.33 to 5.35), the effect of initial chlorine concentration, C_{A_0}, which is one of the main constant parameters in equation 5.36, is diminished. Therefore, although equation 5.37 appears to be a simpler equation than equation 5.36, it may produce results that are greatly sensitive to initial values of its parameters. Consequently, parameter estimation for equation 5.37 is expected to be more problematic than equation 5.36.

Since extended SOM formula is developed based on equation 5.37 and not equation 5.36, and due to the fact that extended version of SOM contains more sophisticated formulation structure with more parameters, it is therefore expected that the parameter estimation issue (convergence issue of the parameters) becomes worse for extended SOM.

5.5. Modified Second Order Model (MSOM)

In order to fix the parameter estimation issue for the extended SOM, the author modified the formulation for the extended SOM. It is proposed to use the structure of equation 5.36 for the extended SOM model instead of equation 5.37.

Assuming that chlorine can be separated into two components each reacting independently and rewriting equations 5.27 and 5.28, chlorine reactions with FRA and SRA could be shown using the following reactions:

$$\mathrm{Cl}_{FRA} + \mathrm{FRA} \xrightarrow{\mathrm{k_{FRA}}} \mathrm{P_1} \qquad (5\cdot 38)$$

$$\mathrm{Cl}_{SRA} + \mathrm{SRA} \xrightarrow{\mathrm{k_{SRA}}} \mathrm{P_2} \qquad (5\cdot 39)$$

As mentioned earlier, in the above reactions, FRA and SRA are the fast and slow reacting agents, Cl_{FRA} is the chlorine component reacting with FRA, Cl_{SRA} is the chlorine component reacting with SRA, k_{FRA} and k_{SRA} are reaction rate constants and $\mathrm{P_1}$ and $\mathrm{P_2}$ are the products of the reactions between two separate chlorine components and FRA and SRA, respectively.

Using equation 5.36 for each above reactions, the following equations can be obtained:

$$\mathrm{Cl}_{FRA}(\mathrm{t}) = \frac{\mathrm{Cl}^0_{FRA} - FRA_0}{1 - \frac{FRA_0}{\mathrm{Cl}^0_{FRA}} e^{-(\mathrm{Cl}^0_{FRA} - FRA_0)k_{FRA}t}} \qquad (5.40)$$

$$\mathrm{Cl}_{SRA}(\mathrm{t}) = \frac{\mathrm{Cl}^0_{SRA} - SRA_0}{1 - \frac{SRA_0}{\mathrm{Cl}^0_{SRA}} e^{-(\mathrm{Cl}^0_{SRA} - SRA_0)k_{SRA}t}} \qquad (5.41)$$

where FRA_0 and SRA_0 are initial concentrations of fast and slow reacting agents and Cl^0_{FRA} and Cl^0_{SRA} are initial concentrations of chlorine components that react with FRA and SRA, respectively.

Assuming $= \frac{\mathrm{Cl}_{FRA}^{0}}{Cl_0}$, the chlorine residual at time t can be predicted as below:

$$Cl(\mathrm{t}) = \frac{ZCl_0 - FRA_0}{1 - \frac{FRA_0}{ZCl_0} e^{-(ZCl_0 - FRA_0)k_{FRA}t}} + \frac{(1-Z)Cl_0 - SRA_0}{1 - \frac{SRA_0}{(1-Z)Cl_0} e^{-((1-Z)Cl_0 - SRA_0)k_{SRA}t}} \qquad (5.42)$$

As highlighted earlier, the modified second order model (MSOM) is developed based on the same principle that PFOM is based on; and that is the possibility of dividing chlorine into two separate parts, each part is assumed to decay independently with its own individual decay rate. However, as mentioned earlier, from a theoretical viewpoint, separating chlorine into two constituents, assuming that one part is being decayed fast whilst the decay of another part is slow, does not appear to be fundamentally valid. Therefore, similar to PFOM, MSOM contains a modelling authenticity issue.

5.6. Assessment of MSOM against Extended SOM

In this section, effectiveness of the MSOM will be evaluated against extended SOM. The criterion for evaluating the effectiveness of the models is considered to be the accuracy of the results the nominated models generate. That is how accurate the nominated models predict the chlorine residuals. The weighted error between experimental and model data (χ^2) can be used as a measure for assessment of the accuracy of the models.

5.6.1. Chlorine Decay Test Data

In order to compare the accuracy of the MSOM with extended SOM, three sets of data have been considered. The first two sets of data are the data obtained from the free chlorine decay test undertaken by Koechling (1998) for the water samples described in Table 5.1. Tables 5.2 and 5.3 show the chlorine decay test data obtained by Koechling (1998) for the water samples described in Table 5.1. The third set of data is selected to be the results of one of chlorine decay tests undertaken by Warton et al. (2006). Table 5.4 shows the water quality characteristics of the water sample used in the experiment undertaken by Warton et al. (2006) and Table 5.5 shows the chlorine decay test data for a water sample tested for multiple dosing between 4 and 10 mg/L (Warton et al., 2006).

Table.5.1 : Water Quality Characteristics of the Water Samples from Koechling (1998)

Sample label	**Description**	**water quality characteristics**		
		DOC (mgL^{-1})	**UVA$_0$ (cm^{-1})**	**Alkalinity (mg/L CaCO$_3$)**
HRW	Hoover Reservoir, OH	3.88	0.129	92
ARW	Ashley Reservoir, MA	3.70	0.157	8

Table.5.2 : Free Chlorine Decay Test Data for Water Sample HRW (Koechling, 1998)

Time (hrs)	**Chlorine Residual (mgL^{-1})**	**Time (hrs)**	**UAV (1/cm)**
0.0	4.58	0.0	0.05995
0.1	4.42	0.1	0.04571
0.3	4.31	0.4	0.04458
0.5	4.20	0.6	0.04397
1.0	4.04	1.0	0.04348
2.0	3.95	2.1	0.04157
4.0	3.67	4.0	0.04042
8.2	3.32	8.2	0.03991
24.2	2.74	24.3	0.03622
48.0	1.91	48.0	0.03451
72.0	1.56	72.0	0.03257
120.0	1.06	120.0	0.03098

Table.5.3 : Free Chlorine Decay Test Data for Water Sample ARW (Koechling, 1998)

Time (hrs)	**Chlorine Residual (mgL^{-1})**	**Time (hrs)**	**UAV (1/cm)**
0.0	2.69	0.0	0.04805
0.1	2.22	0.1	0.03680
0.3	1.94	0.3	0.03434
0.5	1.89	0.5	0.03301
1.0	1.76	1.0	0.03188

2.0	1.56	2.0	0.03088
4.1	1.44	4.1	0.02976
8.0	1.27	8.0	0.02847
25.0	0.91	25.0	0.02649
49.0	0.70	49.0	0.02544
73.8	0.54	73.8	0.02435
120.0	0.35	120.0	0.02342

Table.5.4 : Water Quality Characteristics of the Water Samples from Warton et al. (2006)

Sample label	**Description**	**water quality characteristics**			
		DOC (mgL^{-1})	**UVA_0 (cm^{-1})**	**pH**	**Alkalinity (mg/L $CaCO_3$)**
A.B.W257	Warton et al. (2006)	1.8	0.058	7.97	95

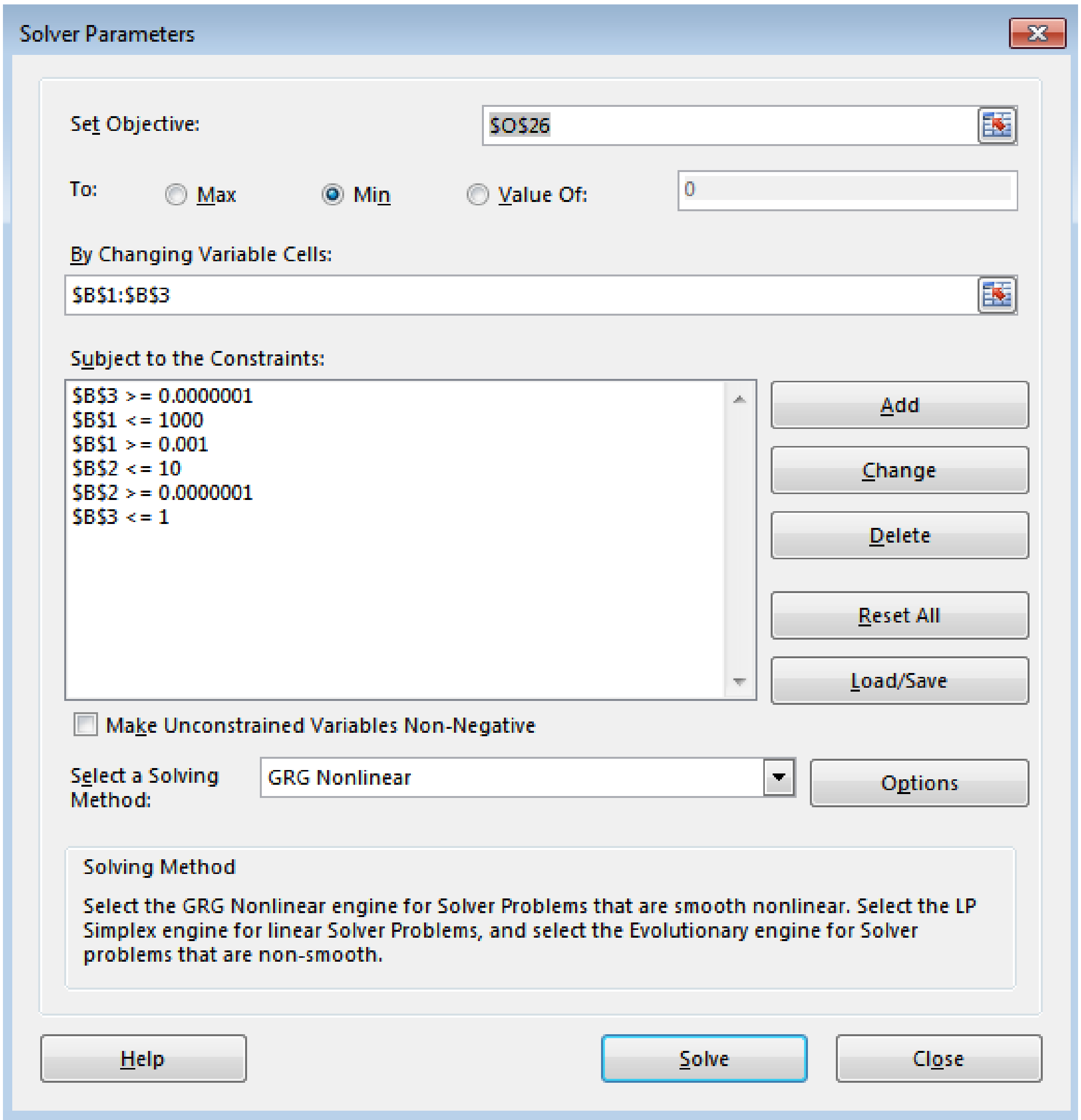
Table.5.5 : Free Chlorine Decay Test Data Obtained from Warton et al. (2006)'s Study

Time (hrs)	**Initial Chlorine Dosing (mg/L)**			
	Cl_0=4 mg/L	**Cl_0=6 mg/L**	**Cl_0=8 mg/L**	**Cl_0=10 mg/L**
0	4.00	6	8	10
0.08	3.25	4.68	6.42	8.09
0.25	2.39	4.05	5.86	7.79
0.5	2.00	3.9	5.78	7.69

1	1.85	3.87	5.69	7.59
1.5	1.78	3.79	5.58	7.59
2	1.70	3.76	5.58	7.54
2.5	1.70	3.6	5.58	7.44
3	1.67	3.6	5.54	7.44
3.5	1.60	3.58	5.5	7.4
4	1.58	3.54	5.41	7.28
21	1.04	3.09	5.06	6.75
30	1.00	3.02	4.98	6.55
50	0.84	2.84	4.66	6.04
72	0.53	2.38	4.17	5.54
96	0.42	2.3	4.17	5.49
101	0.33	2.27	4.01	5.34
120	0.26	2.12	4.01	5.29
144	0.14	1.99	3.89	5.14
168	0.11	1.87	3.77	4.88

5.6.2. Data Analysis

Data analysis for chlorine decay modelling of the selected data have been performed using prepopulated Excel spreadsheets. Solver Add-in is used to undertake parameter estimation for the two nominated modelling approaches (MSOM and extended SOM). Figure 5.1 shows the Excel Solver Parameters Dialog Box.



Set Objective: `$O$26`

To: ○ Max ● Min ○ Value Of: 0

By Changing Variable Cells: `$B$1:$B$3`

Subject to the Constraints:

```
$B$3 >= 0.0000001
$B$1 <= 1000
$B$1 >= 0.001
$B$2 <= 10
$B$2 >= 0.0000001
$B$3 <= 1
```

☐ Make Unconstrained Variables Non-Negative

Select a Solving Method: GRG Nonlinear

Solving Method

Select the GRG Nonlinear engine for Solver Problems that are smooth nonlinear. Select the LP Simplex engine for linear Solver Problems, and select the Evolutionary engine for Solver problems that are non-smooth.

Fig.5.1.: Excel Solver Parameters Dialog Box

For both models (MSOM and extended SOM), the chlorine residuals have been predicted for each data set over the entire retention time with maximum one hour intervals. The sum of squared errors (SSE) between actual and predicted data has been calculated for each data set for both models. The SSEs, which are calculated for each data set, have then been compared between MSOM and Extended SOM to evaluate the models accuracy.

5.6.3. Results and Discussions

Table 5.6 compares the results of chlorine decay modelling and parameter estimation between MSOM and the Extended SOM for water sample HRW from Koechling (1998)'s study. As can be seen from the results, both model predicted exactly the same values for the chlorine residuals, although estimated different values for the model parameters. Therefore, Sum Squared Error (SSE) for both models is equally calculated to be 0.03 and R Squared (R^2) is 0.9988. Having said that, the author found it difficult to conduct the parameter estimation for the extended SOM and had to change the initial values for the model parameters few times for the model results to reach convergence. Table 5.7 shows predicted chlorine decay modelling results and estimated parameters for another water sample ARW from Koechling (1998)'s study using MSOM and the Extended SOM. Similar to the results in Table 5.6, the predicted and measured values for chlorine residuals are very close for both models. Further, both models predicted exact same values for the chlorine residuals. However, again, the parameter estimation for the Extended SOM was found to be more challenging than MSOM.

The convergence issue during parameter estimation for the Extended SOM was even more evident when comparison of the results was made between the two models for chlorine decay modelling for multiple dosing scenario. Tables 5.8 and 5.9 show the results of modelling chlorine decay for a water sample from Warton et al. (2006)'s Study using MSOM and the Extended SOM with four initial chlorine doses of 4, 6, 8 and 10 mg/L. As can be seen from Tables 5.8 and 5.9, SSE values for modelling chlorine decay of the water sample chlorinated with multiple chlorine dosing are 1.7 for MSOM and 41.34 for the Extended SOM. Accordingly, the data fitting of the data for MSOM appears much better than for the Extended SOM as shown in Figures 5.3 and 5.4. In addition, obtaining convergence for parameter estimation for multiple dosing scenario was found to be much more difficult for the Extended SOM compared to the MSOM.

Table.5.6 : MSOM and Extended SOM Predicted Results and Parameter Estimation for Free Chlorine Decay Test Undertaken for Water Sample HRW (Koechling, 1998)

Chlorine Decay Model Name:		MSOM		Extended SOM	
Data Set Name:		HRW (RAW) Water Sample; Koechling (1998)			
Model Parameters		FRA_0	0.771	R_1	1.017
		k_FRA	2.349	R_2	1.169
		SRA_0	4.530	k_1	1.672
		k_SRA	0.004	k_2	0.016
		Z	0.144	Z	0.154
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	4.58	4.58	0.00	4.58	0.00
0.10	4.42	4.47	0.00	4.47	0.00
0.30	4.31	4.32	0.00	4.32	0.00
0.60	4.20	4.18	0.00	4.18	0.00
1.00	4.04	4.06	0.00	4.06	0.00
2.10	3.95	3.88	0.01	3.88	0.01
4.00	3.67	3.68	0.00	3.69	0.00
8.00	3.32	3.40	0.01	3.40	0.01
24.00	2.74	2.65	0.01	2.65	0.01
48.00	1.91	1.97	0.00	1.97	0.00
72.00	1.56	1.55	0.00	1.55	0.00
120.00	1.06	1.05	0.00	1.05	0.00
		Sum Squared Error (SSE)	0.03	Sum Squared Error (SSE)	0.03
		R Squared (R^2)	0.9983	R Squared (R^2)	0.9983

Table.5.7 MSOM and Extended SOM Predicted Results and Parameter Estimation for Free Chlorine Decay Test Undertaken for Water Sample ARW (Koechling, 1998)

Chlorine Decay Model Name:		MSOM		Extended SOM	
Data Set Name:		ARW (RAW) Water Sample; Koechling (1998)			
Model Parameters		FRA$_0$	1.089	R$_1$	1.032
		k_FRA	6.252	R$_2$	0.902
		SRA$_0$	1.475	k$_1$	6.602
		k_SRA	0.022	k$_2$	0.037
		Z	0.392	Z	0.392
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	2.69	2.69	0.00	2.69	0.00
0.10	2.22	2.25	0.00	2.25	0.00
0.30	1.94	1.96	0.00	1.96	0.00
0.50	1.89	1.84	0.00	1.84	0.00
1.00	1.76	1.71	0.00	1.71	0.00
2.00	1.56	1.59	0.00	1.59	0.00
4.10	1.44	1.46	0.00	1.46	0.00
8.00	1.27	1.30	0.00	1.30	0.00
25.00	0.91	0.91	0.00	0.91	0.00
49.00	0.70	0.66	0.00	0.66	0.00
73.80	0.54	0.52	0.00	0.52	0.00
120.00	0.35	0.39	0.00	0.39	0.00
		Sum Squared Error (SSE)	0.01	Sum Squared Error (SSE)	0.01
		R Squared (R^2)	0.9976	R Squared (R^2)	0.9976

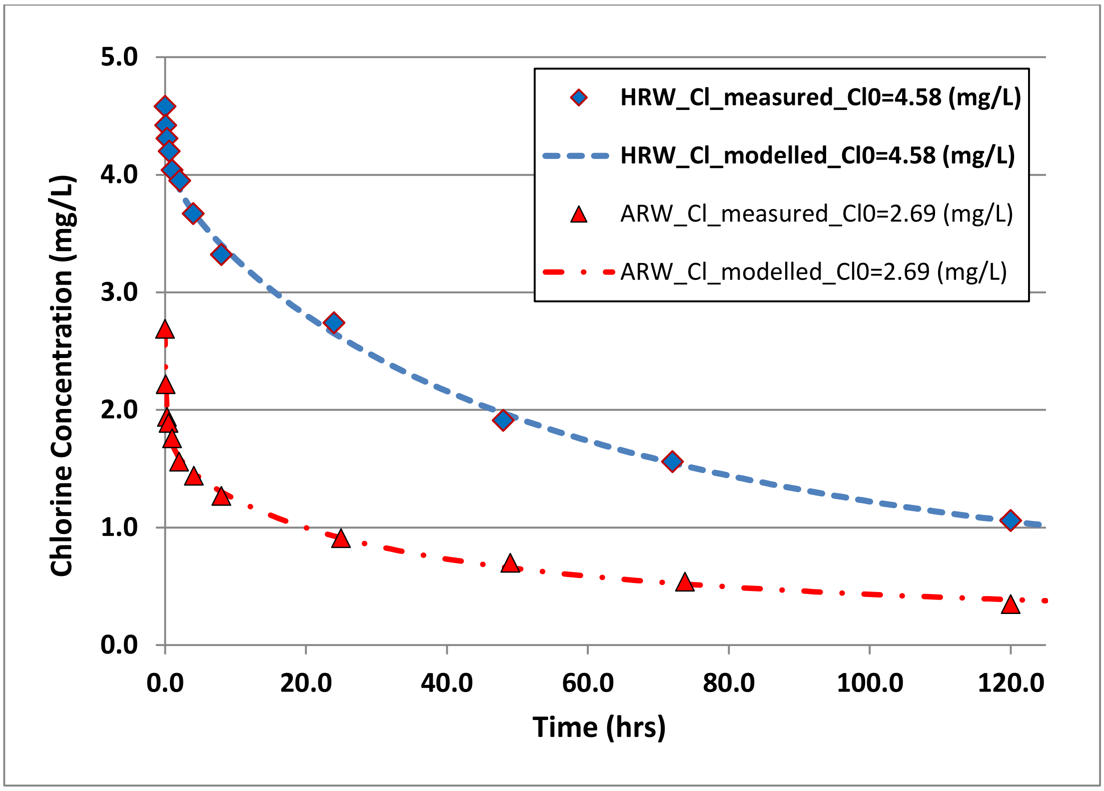


Fig.5.2.: Goodness of data fitting of chlorine decay modelling using MSOM and Extended SOM for water samples HRW and ARW from Koechling (1998)'s study

Table.5.8 MSOM Predicted Results and Parameter Estimation for Free Chlorine Decay Test (Multiple Dosing) Undertaken for Water Sample from Warton et al. (2006)'s Study

Chlorine Decay Model Name:					MSOM				
Data Set Name:					Warton et al. (2006)				
Model Parameters					FRA$_0$				2.344
					k_FRA				3.489
					SRA$_0$				3.140
					k_SRA				0.004
					Z				0.596
time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)				Squared Error
0.0	4.00	6.00	8.00	10.00	4.00	6.00	8.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	3.06	4.72	6.46	8.26	0.07
0.3	2.39	4.05	5.86	7.79	2.40	4.00	5.80	7.70	0.01
0.5	2.00	3.90	5.78	7.69	2.09	3.74	5.65	7.63	0.05
1	1.85	3.87	5.69	7.59	1.87	3.63	5.61	7.60	0.06
2	1.78	3.79	5.58	7.59	1.78	3.61	5.59	7.58	0.03
2	1.70	3.76	5.58	7.54	1.73	3.59	5.57	7.55	0.03
3	1.70	3.60	5.58	7.44	1.69	3.58	5.55	7.53	0.01
3	1.67	3.60	5.54	7.44	1.67	3.56	5.53	7.50	0.01
4	1.60	3.58	5.50	7.40	1.64	3.55	5.51	7.48	0.01
4	1.58	3.54	5.41	7.28	1.62	3.53	5.49	7.45	0.04
21	1.04	3.09	5.06	6.75	1.29	3.12	4.96	6.81	0.08
30	1.00	3.02	4.98	6.55	1.16	2.94	4.74	6.55	0.09
50	0.84	2.84	4.66	6.04	0.95	2.65	4.38	6.14	0.14
72	0.53	2.38	4.17	5.54	0.77	2.41	4.09	5.82	0.14
96	0.42	2.30	4.17	5.49	0.63	2.21	3.86	5.57	0.15
101	0.33	2.27	4.01	5.34	0.60	2.18	3.82	5.53	0.15
120	0.26	2.12	4.01	5.29	0.52	2.07	3.69	5.39	0.18
144	0.14	1.99	3.89	5.14	0.43	1.95	3.56	5.25	0.21
168	0.11	1.87	3.77	4.88	0.36	1.86	3.45	5.15	0.24
	Sum Squared Error (SSE)								1.70
	R Squared (R^2)								0.9944

Table.5.9 Extended SOM Predicted Results and Parameter Estimation for Free Chlorine Decay Test (Multiple Dosing) Undertaken for Water Sample from Warton et al. (2006)'s Study

Chlorine Decay Model Name:	Extended SOM	
Data Set Name:	Warton et al. (2006)	
Model Parameters	R_1	1.008
	R_2	0.457
	k_1	21.598
	k_2	0.015
	Z	0.309

time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)				Squared Error
0.0	4.00	6.00	8.00	10.00	4.00	6.00	8.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	3.21	4.82	6.42	8.03	0.02
0.3	2.39	4.05	5.86	7.79	2.95	4.42	5.90	7.37	0.63
0.5	2.00	3.90	5.78	7.69	2.85	4.28	5.71	7.14	1.19
1	1.85	3.87	5.69	7.59	2.80	4.19	5.59	6.99	1.37
2	1.78	3.79	5.58	7.59	2.77	4.15	5.54	6.92	1.56
2	1.70	3.76	5.58	7.54	2.75	4.12	5.50	6.87	1.68
3	1.70	3.60	5.58	7.44	2.74	4.10	5.47	6.84	1.70
3	1.67	3.60	5.54	7.44	2.72	4.08	5.45	6.81	1.75
4	1.60	3.58	5.50	7.40	2.71	4.07	5.42	6.78	1.86
4	1.58	3.54	5.41	7.28	2.70	4.05	5.40	6.75	1.80
21	1.04	3.09	5.06	6.75	2.44	3.66	4.88	6.10	2.74
30	1.00	3.02	4.98	6.55	2.33	3.50	4.67	5.84	2.62
50	0.84	2.84	4.66	6.04	2.15	3.23	4.31	5.38	2.43
72	0.53	2.38	4.17	5.54	2.01	3.01	4.02	5.02	2.88
96	0.42	2.30	4.17	5.49	1.89	2.84	3.79	4.74	3.18
101	0.33	2.27	4.01	5.34	1.87	2.81	3.75	4.69	3.17
120	0.26	2.12	4.01	5.29	1.81	2.71	3.62	4.52	3.49
144	0.14	1.99	3.89	5.14	1.75	2.62	3.49	4.36	3.73
168	0.11	1.87	3.77	4.88	1.70	2.54	3.39	4.24	3.52
Sum Squared Error (SSE)									41.34
R Squared (R^2)									0.9868

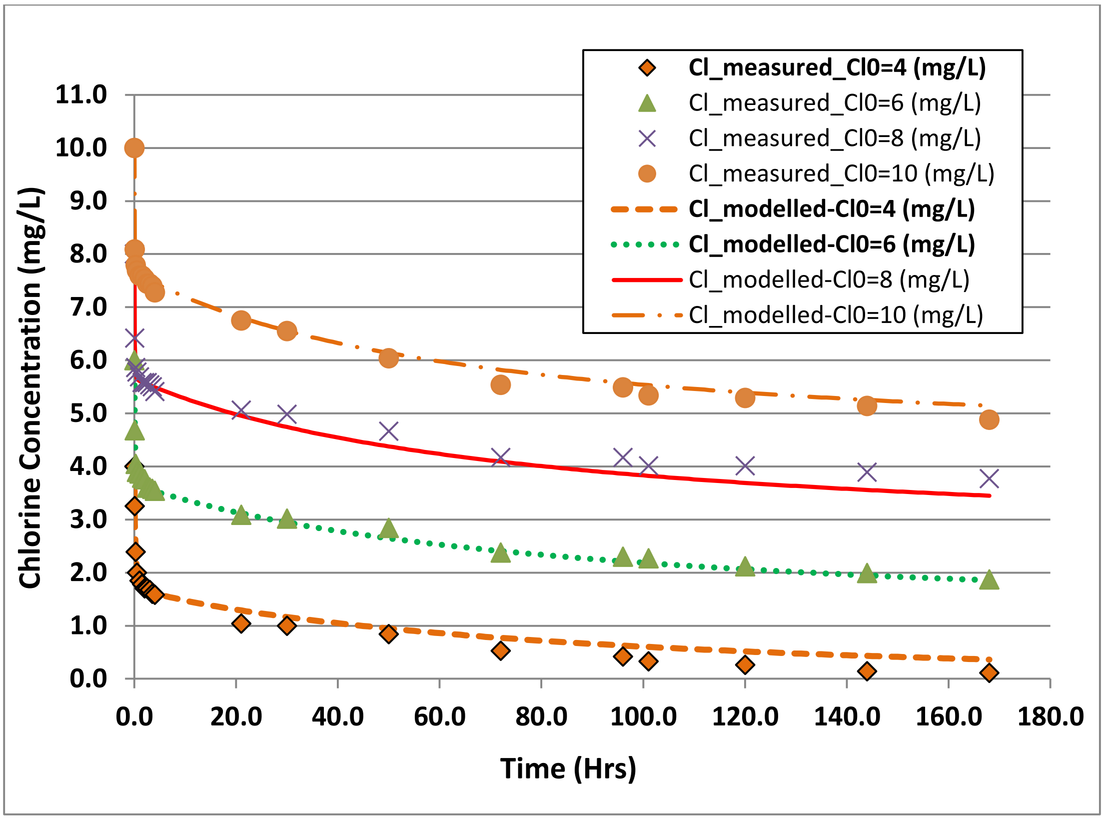


Fig.5.3.: Goodness of data fitting of chlorine decay modelling using MSOM for the water sample from Warton et al. (2006)'s study

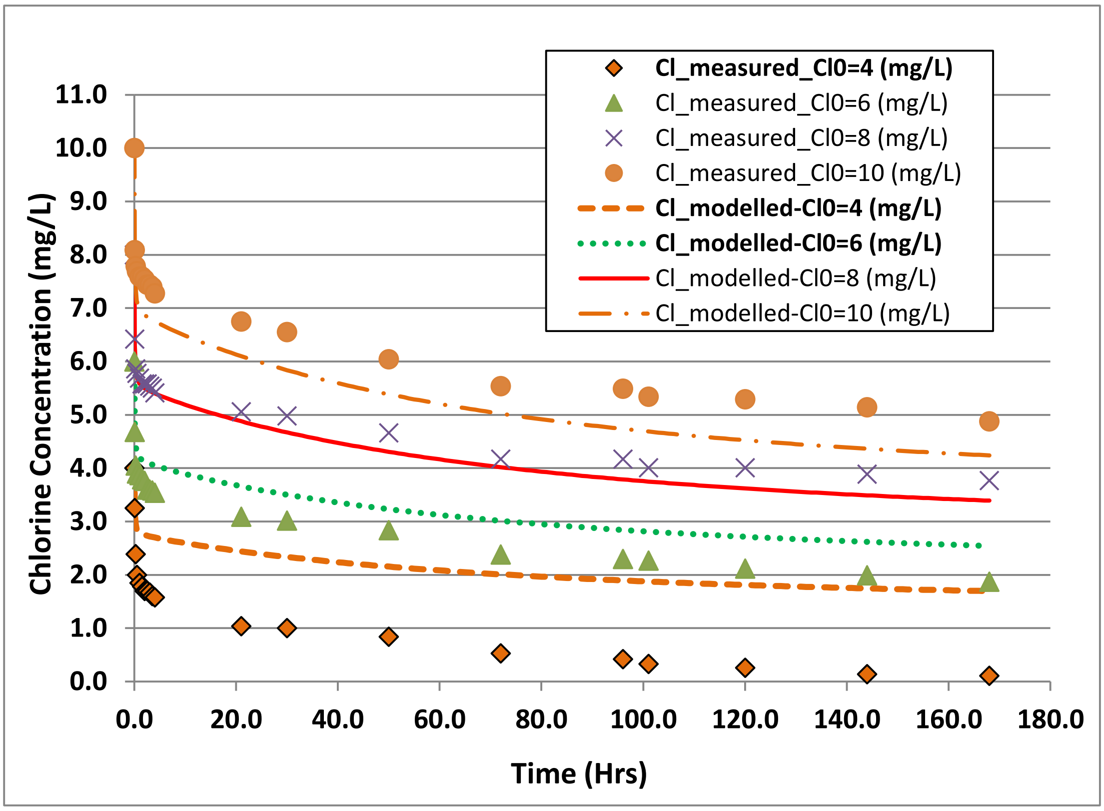


Fig.5.4.: Goodness of data fitting of chlorine decay modelling using Extended SOM for the water sample from Warton et al. (2006)'s study

5.7. Conclusion

Second Order Model (SOM) is one of the well-known process based chlorine decay models that was proposed by Clark and Sivaganesan (1998) in order to improve the accuracy of the results of the chlorine decay models by considering the effect of reacting agents in the process of formulating the modelling mechanisms. Clark and Sivaganesan (2002) proposed an Extended SOM to further improve the accuracy of SOM's predictions using the main principle on which the PFOM was based, which is separating chlorine into two distinct components, each one reacting with a different reacting agent and a different reaction rate. One major issue of the extended second order model (Extended SOM) was found to be the high sensitivity and dependence of the parameter estimation process and convergence on the initial values of model parameters. The issue was clearly explained by Clark and Sivaganesan (2002) and also was investigated by the author. A new model called modified second order model (MSOM) was developed by the author in order to improve the parameter estimation process of the Extended SOM. The results of MSOM and Extended SOM were compared for various literature chlorine decay data including single and multiple dosing scenarios. It was concluded that MSOM and Extended SOM produce the same results when chlorine decay data with single initial chlorine concentration is modelled. However, when chlorine decay data with multiple dosing scenario is used, MSOM showed significant improvement in accuracy of the predicted chlorine residuals compared to the Extended SOM. Moreover, for both single and multiple dosing scenarios, the parameter estimation process and convergence of the solution was found more difficult for the Extended SOM compared to the MSOM.

6. Practical Criteria for Selection of the Chlorine Bulk Decay Models

6.1. Introduction

There are two main objectives/goals that have been defined for disinfection of drinking water supplies. The first objective is mainly to remove harmful microorganisms in drinking water before it reaches any consumers (primary disinfection). The second objective is to maintain a minimum concentration of the disinfecting agent throughout the distribution system to prevent microbial growth and to reduce the effect of potential contamination (secondary disinfection).

Chlorine is believed to be the best candidate amongst all disinfectant agents in achieving both of abovementioned objectives for disinfection of drinking water supplies. Due to its low cost, high efficiency in deactivating bacteria, ease of application and monitoring, till now chlorine is believed to be the most commonly used disinfectant (Hua et al., 1999). However, as a chemical agent, chlorine reacts with many substances and particles in water and on the pipe wall and, as a result, its concentration decreases as it travels through the distribution system. This is known as chlorine decay. As chlorine decays, it loses its potential to effectively achieve the main objectives of disinfection of water in distribution systems (primary and secondary disinfection). In order to overcome this issue more chlorine can be added to water to compensate its decay. However, the amount of chlorine added to the water is very important. If the initial chlorine dosing concentration is too low, there may not be a residual left at the end of the distribution system to protect against reoccurrence of any potential contamination. If the dosing rate is too high, it can lead to customer complaints, corrosion of the pipe network or the formation of by-products, including trihalomethanes (THMs), which are suspected carcinogens.

Therefore, the following main factors/issues associated with chlorination must be considered and adequately addressed in order to effectively achieve the overall goals of disinfection in distribution systems:

6.1.1. Determination of the Adequate Primary Disinfection

Chlorine is a strong oxidant that can oxidize many dissolved inorganic substances and the natural organic matter (NOM) remaining in the water after treatment. As a result, a considerable loss of chlorine occurs due to the reactions between chlorine and these substances. As mentioned earlier, this chlorine loss is referred to as chlorine decay.

The chlorine decay is most rapid immediately after chlorine is added to the water. In many water supply systems, a substantial amount of chlorine is applied to water just before it leaves the treatment plant. The chlorine concentration is then quickly decreasing at the beginning of the distribution system. Due to the fact that the water quality characteristics of the treated water are unknown, the extent of this initial chlorine decay is also not known. Sufficient initial concentration of the chlorine is therefore required to ensure that the remaining chlorine after its initial rapid decay is still adequate. In fact, chlorine does not kill pathogens instantly on contact. The rate of inactivation depends on the following factors:

- The type of pathogen
- Chlorine Concentration, C (mg/L)
- Contact Time, T (min)
- Water Temperature
- pH of Water

Adequate primary disinfection is usually specified in terms of a minimum value of Ct, which is the product of a chlorine concentration (assumed constant) and the time over which this concentration is maintained. In a distribution system, this minimum value should be achieved before water reaches the first consumer. The main issue is that, in practice, quantifying this minimum value is a major challenge. In fact, the actual chorine concentration for the primary disinfection is often obtained using trial and error.

6.1.2. Maintaining Minimum Chorine Residual (Secondary Disinfection)

Most of water quality regulations require water authorities and operators to maintain minimum chlorine residual throughout the distribution system. This minimum chlorine residual is to protect the water network against regrowth of harmful pathogens. Secondary disinfection is, therefore, sometimes considered to be necessary and is adequate if chlorine residuals are maintained at all points in the distribution network, which is sufficient to control the microbial density of the water. Due to chlorine decay, a substantially greater concentration must be established prior to entry to the distribution system (and possibly boosted at intermediate points downstream) to obtain the minimum residual required at the system extremities.

6.1.3. Minimising Chlorinated By-Products

The reaction between chlorine and some of the NOM results in the formation of chlorinated by-products, some of which have been proved to be carcinogenic and harmful to human health. Thus, the total quantity of chlorine demand to achieve primary and secondary disinfection needs to be minimized, so that formation of these by-products and their associated health risks are also minimized. Nitrogenous by-products, such as n-Nitrosodimethylamine (NDMA), are recently discovered to be a major concern. The formation of NDMA depends on organic nitrogen initially present or the combined chlorine formed from it. Therefore, it may also be required to consider minimising combined chlorine formation.

6.1.4. Controlling the Taste and Odour Associated with Chlorination

Some of the reactions between chlorine and NOM produce tastes or odours which are unpleasant to consumers. Prevention of chlorine inducing taste and odours may require a lower dose of chlorine at the head of the system (and any re-chlorination points) than that required to limit by-product formation to acceptable levels.

In this chapter the most practical criteria for the selection of mathematical chlorine decay models to address these issues, which are important for effective planning and management of disinfection in complex water distribution systems, will be discussed. These practical criteria are required for modelling chlorine decay to make the models fit for purpose.

6.2. Practical Criteria for Selection of Chlorine Bulk Decay Models

It has been adequately emphasized and understood that modelling of chlorine decay is required in order to effectively estimate and manage the chlorine residual and its by-products within existing water networks (management application) and also for new systems (planning application). As discussed earlier, there are some requirements that have to be met in order for a chlorine decay model to efficiently estimate the chlorine residual within a distribution system and assist in achieving the planning and management goals of the chlorination.

There are many chlorine bulk decay models within the literature, some of which have been discussed previously. Each model has particular characteristics, capabilities and also weaknesses with regards to meeting the requirements and successfully pursuing the objectives of modelling chlorine decay. Therefore, in order to select the best modelling approach for chlorine decay modelling of a water supply network of interest, firstly, these requirements have to be clearly understood.

6.2.1. Accurate Representation of Chlorine Decay Curve (Accuracy)

One of the most important requirements for a chlorine decay model is to accurately represent the chlorine decay curve for a bulk water sample. Using the simple exponential (first order) model to estimate the chlorine bulk decay separately from the wall decay, recalibration of the full system model is still found to be required. One reason for this is the inability of the simple exponential decay model (i.e., first-order reaction) to accurately represent the chlorine decay curve within a bulk water sample. This may occur over the period of interest (between initial dosing and reaching the system extremity), over the range of initial doses of interest, or over the annual temperature range.

In addition, any inaccuracy in the prediction of the bulk decay generates the same but opposite error in the estimate of the wall decay. The differences between the modelled and actual bulk decay rate, including those resulting from the inaccuracies of the bulk decay model, are therefore fundamentally related with the wall decay estimates. In other words, higher accuracy in bulk decay models will enhance the accuracy of wall decay estimates. Therefore, it is important that the models predicting the chlorine bulk decay are as accurate as possible in order to minimise the total error and inaccuracies of the modelling results and predictions.

Another reason for having more accurate models is because detailed monitoring of chlorine residuals at the ends of distribution systems is usually vital to maintain effective secondary disinfection. Sufficient and effective secondary disinfection of the distribution system will be achieved when a minimum (usually between 0.2 to 0.5 mg/L) residual is maintained at the furthest points of the system. This will require accurate prediction/estimation of small residuals at the longest retention times. Therefore, accurate modelling and characterization of bulk decay over the full retention time of a water network system (up to two weeks in large networks) is required in order to obtain correct information and results for management and planning applications.

One can question how much accuracy a chlorine bulk decay model will need to be considered as a model with satisfactory level of accuracy in estimating the chlorine residuals. An answer to this question might be the more accurate the model results will be, the better the model is. Although at first glance this answer may appear a good solution for accuracy requirement of the chlorine decay models, it may also compromise another requirement of the chlorine decay modelling approach, i.e. simplicity of the model, which will be discussed later. It is more likely that complex modelling methods result in more accurate predictions for chlorine residuals in the bulk water. However, complex models with more parameters to be estimated/calibrated will make the modelling approach more complicated as well. Therefore, it makes more sense to obtain a upper limit for the accuracy requirement of the models as general guidance.

One method to quantify the accuracy requirement is to use the values recommended by Australian Drinking Water Guidelines for minimum required free chlorine residual in the distribution system. In accordance with Australian Drinking Water Guidelines, 2011, the amount of chlorine residual required varies with the flow rate, the quality of the raw water and other factors. However, generally, a free chlorine residual of between 0.2 and 0.5 mg/L will be adequate at the customer end of the distribution system (Australian drinking water guidelines, 2011). Therefore, considering values between 0.05 and 0.1 mg/L as the minimum accuracy for a chlorine decay model would be reasonable. Having said that, measurement of very low chlorine residuals during a lab test would be required in order to evaluate the model accuracy based on the above mentioned method. Also, it would be difficult to regulate this method appropriately for all scenarios and situations and for wide range of models.

Another method, however, is to calculate the sum of errors between the modelled/predicted and the measured values. The weighted error (sum of errors or chi^2- chi squared) between experimental and model data (χ^2) can be used as a measure of accuracy of the proposed chlorine decay model which can be defined as follows:

$$\chi^2(\mathrm{p}) = \sum_{\mathrm{i}=1}^{\mathrm{n}} \left(\frac{\mathrm{f}_{\mathrm{meas,i}} - \mathrm{f}_{\mathrm{i}}(\mathrm{p})}{\sigma_{\mathrm{meas,i}}}\right)^2 \qquad (6 \cdot 1)$$

where $\mathrm{f}_{\mathrm{meas,i}}$ is the ith measured value, $\mathrm{f}_{\mathrm{i}}(\mathrm{p})$ is the calculated value from the model using parameter values p and $\sigma_{\mathrm{meas,i}}$ is the estimated standard deviation of $\mathrm{f}_{\mathrm{meas,i}}$.

In order to efficiently compare the accuracy of the models, however, the error analysis performed with individual chlorine decay data set will not be adequate to represent the accuracy of a nominated model against other chlorine decay models. Hence, analysis of errors must be undertaken using adequate number of data sets and in different situations/scenarios including multiple dosing scenarios and change in water quality.

6.2.2. Simplicity of the Chlorine Decay Model

Simplicity of a chlorine decay modelling approach is one of the main practical criteria for chlorine decay modelling that has been given great emphasis and attention in the literature. Simplicity of a chlorine decay model has two main aspects. One aspect is the number of model parameters that need to be estimated for calculation of chlorine residuals. Another aspect for the simplicity of a model is whether or not the model has an analytical solution that can be used for calculation of chlorine residuals.

Both data and process-based chlorine decay models would have a number of parameters that need to be estimated prior or during the process of calculating chlorine residuals in the bulk water. Having greater number of parameters for the chlorine decay models would increase the chance of having higher errors during the parameter estimation process. This is because having more parameters would provide the equations involved in parameter estimation with higher degrees of freedom. This would give various parameters a chance to yield different values each time they are run/processed for parameter estimation.

Moreover, having more parameters to be estimated means more effort in calibration of the model in different situations (temperature variations, multiple dosing, change in water quality, etc.) may be required. This will increase the complexity of the modelling approach.

On the other hand, inclusion of more equations and parameters in a chlorine decay model would increase the accuracy in estimating of chlorine residuals. This is simply due to the fact that using more variables in a mathematical model will increase its flexibility in fitting the data that feeds the model. Therefore, there will be a trade-off between the number of parameters used in a chlorine decay model and the accuracy of its chlorine residual estimation results.

Having an analytical solution would also make a chlorine decay model simpler when compared with similar models with no analytical solutions. Without an analytical solution, numerical methods need to be employed in order to perform the parameter estimation, solve the chlorine decay model and finally calculate the chlorine residuals at a given time. This means more time and greater number of iterations are required for convergence of the model solution if no analytical solution exists. However, if analytical solution is available for a model, the model can be solved/converged faster without numerical methods. Moreover, availability of analytical solution would enable the chlorine decay model to be solved without requiring specialist software package. For instance, a simple Excel spread sheet equipped with Solver Add-Ins can be used to perform the parameter estimation of a chlorine decay model with an analytical solution.

6.2.3. Authenticity of the Chlorine Decay Model

Authenticity of a chlorine decay model refers to whether or not the model follows the principles on which the model has been based. Usually models are developed based on one or number of some physical, chemical or mathematical principles, theories and/or facts. Sometimes, assumptions have to be considered in order to simplify the models. It is important, however, that the assumptions made for simplifying a model is reasonable and not contradicting the principle the model is already developed based upon. For instance, first order chlorine decay model (FOM) is based on first order kinetics for chemical decay/decomposition of one substance (here chlorine). It is assumed, however, that the impact of chlorine reactions with other substances in water can be ignored. In fact, in developing FOM, it is assumed that chlorine reacts with only one compound/reactant with excessive concentration so that its reaction with chlorine does not change its concentration considerably. Consequently, FOM completely ignores the existence of other substances reacting with chlorine. Although it is not likely that this assumption becomes plausible, the assumption is not theoretically invalid. Therefore, FOM can be considered as an authentic chlorine decay model.

For development of second order model (SOM), it is assumed that only one agent, which represents all reacting substances in water, reacts with chlorine. Basically, SOM ignores the fact that chlorine may be involved in several concurrent or consecutive reactions with other substances in water. Again, this assumption may not be very likely to become possible but yet it is a valid assumption. Thus, SOM may also be considered as an authentic model.

According to the parallel first order model (PFOM), chlorine is hypothetically divided into two parts, each part is assumed to decay independently according to first order kinetics with its own individual decay rate. From a theoretical viewpoint, separating chlorine into two constituents, assuming that one part is being decayed fast whilst the decay of another part is slow, does not appear to be fundamentally valid. As a result, PFOM cannot be considered as an authentic model.

6.2.4. Ability to Accurately Model Multiple Dosing Scenarios

One of the most important criteria for adequately modelling chlorine decay is the ability of the model to accurately represent the multiple dosing scenarios. As discussed earlier, primary chlorination usually occurs at the end of water treatment process where treated water enters distribution system. The initial chlorine concentration during chlorination, however, may not be accurately known. One of the reasons for not knowing the initial chlorine concentration is that water quality characteristics and therefore initial chlorine demand and CT values may change during treatment process. Another reason may be the need for temporarily increasing the chlorine dose due to maintenance requirements. Also, initial chlorine doses may need to be changed due to temperature variation or due to altering water treatment processes. Consequently, it is important for chlorine decay model to be able to predict the chlorine residuals at various locations of the water distribution system with changing chlorine doses. In order to test a chlorine decay model against this criterion, accuracy of the model in predicting the chlorine residuals in bulk water for multiple chlorine dosing scenario needs to be evaluated.

6.2.5. Ability to Accurately Model Temperature Variation

Temperature variation is one of the important factors that influence the rate of chlorine decay. Annual temperature variation of more than 20°C for water in distribution systems is common. Therefore, chlorine dosing needs to be adjusted substantially between seasons to maintain residuals within desired limits. As a result, the impact from seasonal temperature variation of water should be managed with chlorine decay models. In fact, the chlorine decay models should be able to predict chlorine residuals accurately during various seasons of the year and with different water temperature.

The adjustment of initial chlorine dosing due to seasonal temperature variation does not normally occur within a short period of time and, thus, the impact cannot be dealt with using the multiple dosing scenario. However, Arrhenius equation can be used to estimate the effects of temperature variation on chlorine decay. This can be done by including temperature dependence parameter, i.e. activation energy (E)/universal gas constant (R), in formulation of the chlorine decay models. It is an important criterion for chlorine decay models to be able to accurately model temperature variation effects on chlorine decay.

6.2.6. Meaningful Correlation between Model Parameters and Water Quality Characteristics

As discussed in previous chapters, chlorine decay characteristics in bulk water can be greatly influenced by variation of water quality. Modification of water treatment processes may also change the chlorine demand for treated water. As a result, values of chlorine decay model parameters can change due to varying water quality characteristics. It is therefore important for a chlorine decay model to present a meaningful correlation between its model parameters and the water quality characteristics of its corresponding water sample.

6.2.7. Predicting Chlorine Decay in Blended Waters

During recent years, frequent occurrence of drought events and the impact from climate change have limited the availability of drinking water supplies that are sourced from local catchments and groundwater basins. This has forced government and public agencies to initiate development of seawater desalination plants in many urban areas to compensate for drinking water shortage. In many distribution systems, desalinated water and treated ground or surface water will need to be mixed before they reach the end customer. The blended water may have different chlorine decay demand and behaviour than desalinated or ground/surface treated waters. It is therefore important for chlorine decay models to accurately predict the chlorine decay behaviour for those blended waters.

6.2.8. Modelling Re-Chlorination

Re-chlorination is the injection of chlorine into water, following previous chlorination at the treatment plant, at one or more locations in the distribution system. In many water distribution systems, booster chlorination is required to be operated at some locations within the network in order to maintain the chlorine residuals and satisfy the secondary chlorination requirements. This additional chlorine will boost the amount of chlorine residual at the middle of distribution system. Due to the fact that re-chlorination is usually required in large distribution systems, it is important for chlorine decay models to be able to accurately predict chlorine residuals after re-chlorination.

6.3. Conclusion

In this chapter, initially some of the common issues for modelling chlorine decay within distribution systems for various planning and management application were discussed. Also, the most practical criteria for the selection of mathematical chlorine decay models to address the chlorine decay modelling issues, were highlighted. These practical criteria, which are required for modelling chlorine decay to make the models fit for purpose, are summarised as below:

- Accurate Representation of Chlorine Decay Curve (Accuracy)
- Simplicity of the Chlorine Decay Model
- Authenticity of the Chlorine Decay Model
- Ability to Accurately Model Multiple Dosing Scenarios
- Ability to Accurately Model Temperature Variation
- Meaningful Correlation between Model Parameters and Water Quality Characteristics
- Predicting Chlorine Decay in Blended Waters
- Modelling Re-Chlorination

In the following chapters, some of the abovementioned criteria for selection of the chlorine decay models will be investigated in more details.

7. Comparison of the Accuracy of the Process-Based Chlorine Decay Models for Single Dosing Scenario

7.1. Introduction

As mentioned earlier, one of the practical criteria for selection of the chlorine decay model is accurate representation of the chlorine decay behaviour. In order to compare the accuracy of different models the weighted error (sum of errors or chi^2- chi squared) between experimental and model data (χ^2) can be used as a measure of accuracy of the a chlorine decay model. The weighted error (sum of errors or chi^2- chi squared) can be defined as follows:

$$\chi^2(\mathrm{p}) = \sum_{\mathrm{i}=1}^{\mathrm{n}} \left(\frac{\mathrm{f}_{\mathrm{meas\_i}} - \mathrm{f}_{\mathrm{i}}(\mathrm{p})}{\sigma_{\mathrm{meas\_i}}}\right)^2 \tag{7.1}$$

where $\mathrm{f}_{\mathrm{meas\_i}}$ is the ith measured value, $\mathrm{f}_{\mathrm{i}}(\mathrm{p})$ is the calculated value from the model using parameter values p and $\sigma_{\mathrm{meas\_i}}$ is the estimated standard deviation of $\mathrm{f}_{\mathrm{meas\_i}}$.

As explained before, the error analysis performed using individual chlorine decay data set will not be adequate to represent the accuracy of a nominated model against other chlorine decay models. Hence, analysis of errors must be undertaken using adequate number of data sets and in different situations/scenarios including multiple dosing scenarios and change in water quality.

In this chapter, four already well known process-based chlorine decay models as well as the modified parallel fist order model (MPFOM) and the modified second order model (MSOM) will be evaluated for the accuracy of their results for single dosing scenario.

7.2. Process-Based Chlorine Decay Models:

The following process-based chlorine decay models will be evaluated for their compliance against the accuracy criterion:

- First Order Model (FOM)
- Parallel First Order Model (PFOM)
- Modified Parallel First Order Model (MPFOM)
- Second Order Model (SOM)
- Modified Second Order Model (MSOM)
- Parallel Second Order Model (PSOM)

7.2.1. First Order Model (FOM)

One of the earliest, simplest and initially most popular theoretical (process based) chlorine decay models for modelling chlorine decay in bulk water has been the first order model (FOM). Based on first order kinetics, only one component is involved in the reaction scheme; i.e. compound A is converted to compound B (A→B). In fact, the reaction rate for FOM is only proportionate to the first power of the concentration of the reactant. Using first order kinetics, chlorine concentration is assumed to be decreased over time by itself. In other words, FOM does not take into account the effect of other species with which chlorine is reacting.

Table 7.1 shows the main features of FOM:

Table.7.1 : Main Features of the First Order Model (FOM)

Name of process-based chlorine decay model	Number of parameters	Decay Kinetics	Analytical Solution	Boundary Conditions
First Order Model (FOM)	**1**	$\frac{dCl}{dt} = -k * Cl$	$Cl(t) = Cl_0 \exp(-kt)$	$t \longrightarrow 0 \Rightarrow Cl(t) \longrightarrow Cl_0$ $t \longrightarrow \infty \Rightarrow Cl(t) \longrightarrow 0$

7.2.2. Parallel First Order Model (PFOM)

The parallel first order model (PFOM) has been developed based on the assumption that chlorine decay may proceed through two general parallel reactions between chlorine and two other notional reactants in water. In their model, component X (an unknown portion of free chlorine in water) with concentration C_0x, is assumed to decay according to first order kinetics with a rate constant of k_1 and the remainder, which is the initial chlorine residual without component X with concentration of $C_0(1-x)$, is subject to first order decay with a rate constant of k_2. By definition, x is limited to a range between zero and unity

Table 7.2 shows the main features of PFOM:

Table.7.2 : Main Features of the Parallel First Order Model (PFOM)

Name of process-based chlorine decay model	Number of parameters	Decay Kinetics	Analytical Solution	Boundary Conditions
Parallel First Order Model (PFOM)	**3**	$\frac{dCl_{FRA}}{dt} = -k_{FRA} * Cl_{FRA}$ $\frac{dCl_{SRA}}{dt} = -k_{SRA} * Cl_{SRA}$ $Cl(t) = Cl_{FRA}(t) + Cl_{SRA}(t)$	$Cl(t) = Cl_0 x e^{-k_{FRA} t} + Cl_0(1-x)e^{-k_{SRA} t}$	$t \longrightarrow 0 \Rightarrow Cl(t) \longrightarrow Cl_0$ $t \longrightarrow \infty \Rightarrow Cl(t) \longrightarrow 0$

7.2.3. *Modified Parallel Frist Order Model (MPFOM)*

Considering the impact of other reactants on chlorine decay, PFOM can be modified to include the impact of other reactants. The new chlorine decay model, which is referred to the modified parallel first order model (MPFOM), consists of two simultaneous parallel reactions with the overall second order kinetics as follows:

$$\mathrm{Cl} + \mathrm{FRA} \xrightarrow{\mathrm{k_{FRA}}} \mathrm{P_1} \qquad (7\cdot 2)$$

$$\mathrm{Cl} + \mathrm{SRA} \xrightarrow{\mathrm{k_{SRA}}} \mathrm{P_2} \qquad (7\cdot 3)$$

In the above reactions, Cl is the chlorine agent, FRA and SRA are the fast and slow reacting agents and $\mathrm{P_1}$ and $\mathrm{P_2}$ are the products of the reactions between chlorine and FRA and SRA, respectively. According to the first order kinetics for the above reactions:

$$\frac{\mathrm{dC_{\mathbf{FRA}}}}{\mathrm{dt}} = -\mathrm{k_{\mathbf{FRA}}} * \mathrm{C_{\mathbf{FRA}}} \qquad (7\cdot 4)$$

$$\rightarrow\ \mathrm{C_{FRA}} = \mathrm{C_{FRA_0}} e^{-\mathrm{k_{\mathbf{FRA}}} t} \qquad (7\cdot 5)$$

$$\frac{\mathrm{dC_{\mathbf{SRA}}}}{\mathrm{dt}} = -\mathrm{k_{\mathbf{SRA}}} * \mathrm{C_{\mathbf{SRA}}} \qquad (7\cdot 6)$$

$$\rightarrow\ \mathrm{C_{SRA}} = \mathrm{C_{SRA_0}} e^{-\mathrm{k_{\mathbf{SRA}}} t} \qquad (7\cdot 7)$$

where $\mathrm{C_{FRA}}$ and $\mathrm{C_{SRA}}$ are the concentrations of FRA and SRA in [mg/L] and $\mathrm{k_{FRA}}$ and $\mathrm{k_{SRA}}$ are the rate constants of the FRA and SRA reactions in [$\mathrm{h^{-1}(mg/L)^{-1}}$], respectively.

The following analytical solution formula can be derived mathematically for MPFOM:

$$\mathrm{C_{Cl}} = \mathrm{C_{Cl_0}} - \mathrm{C_{FRA_0}}\left(1 - e^{-\mathrm{k_{\mathbf{FRA}}} t}\right) - \mathrm{C_{SRA_0}}\left(1 - e^{-\mathrm{k_{\mathbf{SRA}}} t}\right) \qquad (7\cdot 8)$$

where $\mathrm{C_{Cl_0}}$ is the initial chlorine concertation, $\mathrm{C_{FRA_0}}$ and $\mathrm{C_{SRA_0}}$ are the initial concentrations of FRA and SRA; and $\mathrm{k_{\mathbf{FRA}}}$ and $\mathrm{k_{\mathbf{SRA}}}$ are the rate constants for the fast and slow reactions respectively.

Table 7.3 shows the main features of MPFOM:

Table.7.3 : Main Features of the Modified Parallel First Order Model (MPFOM)

Name of process-based chlorine decay model	Number of parameters	Decay Kinetics	Analytical Solution	Boundary Conditions
Modified Parallel First Order Model (MPFOM)	4	$\frac{dC_{FRA}}{dt} = -k_{FRA} * C_{FRA}$ $\frac{dC_{SRA}}{dt} = -k_{SRA} * C_{SRA}$	$C_{Cl} = C_{Cl_0} - C_{FRA_0}(1 - e^{-k_{FRA}t})$ $-C_{SRA_0}(1 - e^{-k_{SRA}t})$	$t \rightarrow 0 \Rightarrow Cl(t) \rightarrow Cl_0$ $t \rightarrow \infty \Rightarrow Cl(t) \rightarrow Cl_0 - C_{B0}^1 - C_{B0}^2$

7.2.4. Second Order Model (SOM)

The Second Order Model (SOM) is a two-component second-order chlorine decay model proposed by Clark and Sivaganesan (1998) and is based on a hypothetical reaction between chlorine and another notional substance:

$$aA + bB \rightarrow pP \tag{7.9}$$

where A represents chlorine and B represents all individual organic and inorganic substances that could potentially react with chlorine. P represents the product of the reaction and a, b and p are the stoichiometry parameters. Clark and Sivaganesan (1998) proposed an analytical solution for this model, which appears to be the first successful analytical solution for the second-order model:

$$C_A = \frac{K}{1 - Re^{-ut}} \tag{7.10}$$

where C_A is the initial chlorine concentration and K, R and u are constant parameters that need to be estimated.

Due to the fact that chlorine reacts with many organic and inorganic compounds with various mechanisms and stoichiometry, having stoichiometry parameters does not appear to be appropriate. Therefore, Clark's equation can be modified using simple stoichiometry for the chlorine reaction:

$$Cl_2 + A \overset{k}{\rightarrow} \text{inert product} \tag{7.11}$$

$$Cl(t) = \frac{Cl_0 - C_{A_0}}{1 - \frac{C_{A_0}}{Cl_0} * e^{-(Cl_0 - C_{A_0}) * k * t}} \tag{7.12}$$

where Cl_0 and C_{A_0} are initial concentrations of chlorine and the notional reactant respectively and k is the rate coefficient.

Table 7.4 shows the main features of SOM:

Table.7.4 : Main Features of the Second Order Model (SOM)

Name of process-based chlorine decay model	Number of parameters	Decay Kinetics	Analytical Solution	Boundary Conditions
Second Order Model (SOM)	**2**	$\frac{\mathrm{dCl}}{\mathrm{dt}} = -\mathrm{k} * \mathrm{Cl} * \mathrm{A}$	$Cl(\mathrm{t}) = \frac{\mathrm{Cl_0 - C_{A_0}}}{1 - \frac{\mathrm{C_{A_0}}}{\mathrm{Cl_0}} * \mathrm{e}^{-(\mathrm{Cl_0 - C_{A_0}}) * \mathrm{k} * \mathrm{t}}}$	$\mathrm{t} \longrightarrow 0 \ \Rightarrow \mathrm{Cl(t)} \longrightarrow \mathrm{Cl_0}$ $\mathrm{t} \longrightarrow \infty \ \Rightarrow \mathrm{Cl(t)} \longrightarrow \mathrm{Cl_0 - C_{A_0}}$

7.2.5. *Modified Second Order Model (MSOM)*

Clark and Sivaganesan (2002) extended their model (Clark and Sivaganesan, 1998) to include both fast and slow reaction types by separating chlorine into two components, each reacting with a single organic constituent separately. In fact, Clark and Sivaganesan (2002) combined concepts of SOM and PFOM and proposed a new chlorine decay model (Referred to Extended SOM) in order to rectify the shortcomings of both SOM and PFOM. Extended SOM formulation can be summarized as below:

$$C_A^1(\mathrm{t}) = \frac{\mathrm{C\,l}_0^1(1 - R_1)}{1 - \mathrm{R}_1\mathrm{e}^{-(1-R_1)k_1 t}} \tag{7.13}$$

$$C_A^2(\mathrm{t}) = \frac{\mathrm{C\,l}_0^2(1 - R_2)}{1 - \mathrm{R}_2\mathrm{e}^{-(1-R_2)k_2 t}} \tag{7.14}$$

where $\mathrm{C\,l}_0^1$ and $\mathrm{C\,l}_0^2$ are initial concentrations of C_A^1 and C_A^2. $C_A^1(\mathrm{t})$ and $C_A^2(\mathrm{t})$ are changes in concentrations of C_A^1 and C_A^2 with time t and R_1, R_2, k_1 and k_2 are parameters to be estimated.

Based on this model, the total initial chlorine concentration at time t=0 (Cl_0) can be considered as sum of $\mathrm{C\,l}_0^1$ and $\mathrm{C\,l}_0^2$:

$$Cl_0 = \mathrm{C\,l}_0^1 + \mathrm{C\,l}_0^2 \tag{7.15}$$

Assuming $= \frac{\mathrm{C\,l}_0^1}{Cl_0}$, the chlorine residual at time t can be predicted as below:

$$Cl(\mathrm{t}) = \frac{\mathrm{Cl}_0 Z(1 - R_1)}{1 - \mathrm{R}_1\mathrm{e}^{-(1-R_1)k_1 t}} + \frac{\mathrm{Cl}_0(1 - Z)(1 - R_2)}{1 - \mathrm{R}_2\mathrm{e}^{-(1-R_2)k_2 t}} \tag{7.16}$$

where $Cl(\mathrm{t})$ is the chlorine concentration at time t and Z, R_1, R_2, k_1 and k_2 are unknown parameters.

One of the issues of the Extended SOM was found to be the high sensitivity and dependence of the solutions to the initial values of the model parameters which made the convergence of the solution difficult. To resolve this issue, the author proposed a new model called the modified second order model (MSOM). MSOM contains a modified version of the model formulation which makes the solution of the model less dependent on the initial values of the model parameters. Table 7.5 shows the main features of MSOM:

Table.7.5 : Main Features of the Modified Second Order Model (MSOM)

Name of process-based chlorine decay model	**Number of parameters**	**Decay Kinetics**	**Analytical Solution**	**Boundary Conditions**
Modified Second Order Model (MSOM)	**5**	$\frac{dC_{FRA}}{dt} = -k_{FRA} * C_{CL} * C_{FRA}$ $\frac{dC_{SRA}}{dt} = -k_{SRA} * C_{CL} * C_{SRA}$ $Cl(t) = Cl_{FRA}(t) + Cl_{SRA}(t)$	$Cl(t) = \frac{ZCl_0 - FRA_0}{1 - \frac{FRA_0}{ZCl_0} e^{-(ZCl_0 - FRA_0)k_{FRA}t}} +$ $\frac{(1-Z)Cl_0 - SRA_0}{1 - \frac{SRA_0}{(1-Z)Cl_0} e^{-((1-Z)Cl_0 - SRA_0)k_{SRA}t}}$	$t \to 0 \Rightarrow Cl(t) \to Cl_0$ $t \to \infty \Rightarrow Cl(t) \to C_{Cl_0} - C_{FRA_0} - C_{SRA_0}$

7.2.6. Parallel Second Order Model (PSOM)

Simple format of the Parallel Second Order Model can be described using the following reactions:

$$CL + FRA \xrightarrow{k_{FRA}} P_1 \tag{7.17}$$

$$CL + SRA \xrightarrow{k_{SRA}} P_2 \tag{7.18}$$

In these reactions, Cl is chlorine concentration, FRA is the Fast reacting Reducing Agents, SRA is the Slow reacting Reducing Agents and P_1 and P_2 represent inactive chlorinated by-products. k_{FRA} and k_{SRA} are the rate constants of the reactions.

Following Clark's formulation (1998) and according to second order kinetics for both above reactions, the following can be shown:

$$\frac{dC_{FRA}}{dt} = -k_{FRA} * C_{CL} * C_{FRA} \tag{7.19}$$

$$\frac{dC_{SRA}}{dt} = -k_{SRA} * C_{CL} * C_{SRA} \tag{7.20}$$

$$\frac{dC_{CL}}{dt} = \frac{dC_{FRA}}{dt} + \frac{dC_{SRA}}{dt} = -k_{FRA} * C_{CL} * C_{FRA} - k_{SRA} * C_{CL} * C_{SRA} \tag{7.21}$$

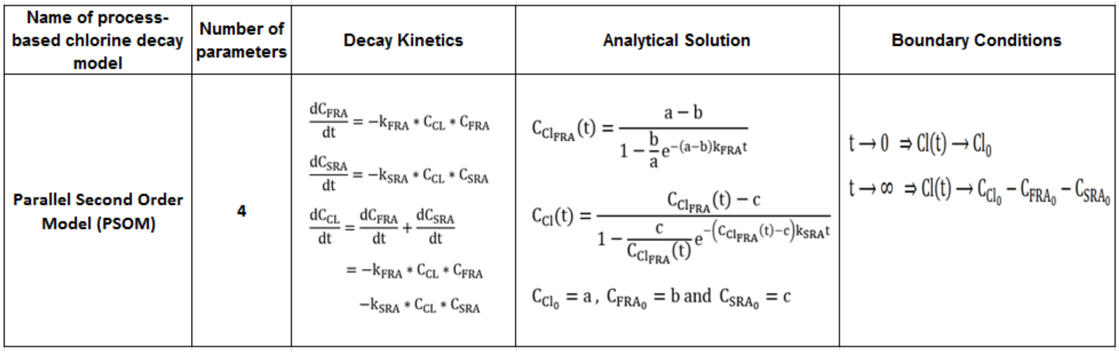
Considering $C_{Cl_0} = a$. $C_{FRA_0} = b$ and $C_{SRA_0} = c$, the following formulas have been obtained for PSOM:

$$C_{Cl_{FRA}}(t) = \frac{a - b}{1 - \frac{b}{a} e^{-(a-b)k_{FRA}t}} \tag{7.22}$$

$$C_{Cl}(t) = \frac{C_{Cl_{FRA}}(t) - c}{1 - \frac{c}{C_{Cl_{FRA}}(t)} e^{-\left(C_{Cl_{FRA}}(t) - c\right)k_{SRA}t}} \tag{7.23}$$

Table 7.6 shows the main features of PSOM:

Table.7.6 : Main Features of the Parallel Second Order Model (PSOM)



Name of process-based chlorine decay model	Number of parameters	Decay Kinetics	Analytical Solution	Boundary Conditions
Parallel Second Order Model (PSOM)	**4**	$\frac{dC_{FRA}}{dt} = -k_{FRA} * C_{CL} * C_{FRA}$ $\frac{dC_{SRA}}{dt} = -k_{SRA} * C_{CL} * C_{SRA}$ $\frac{dC_{CL}}{dt} = \frac{dC_{FRA}}{dt} + \frac{dC_{SRA}}{dt}$ $= -k_{FRA} * C_{CL} * C_{FRA}$ $-k_{SRA} * C_{CL} * C_{SRA}$	$C_{Cl_{FRA}}(t) = \frac{a - b}{1 - \frac{b}{a} e^{-(a-b)k_{FRA}t}}$ $C_{Cl}(t) = \frac{C_{Cl_{FRA}}(t) - c}{1 - \frac{c}{C_{Cl_{FRA}}(t)} e^{-\left(C_{Cl_{FRA}}(t) - c\right)k_{SRA}t}}$ $C_{Cl_0} = a$, $C_{FRA_0} = b$ and $C_{SRA_0} = c$	$t \to 0 \Rightarrow Cl(t) \to Cl_0$ $t \to \infty \Rightarrow Cl(t) \to C_{Cl_0} - C_{FRA_0} - C_{SRA_0}$

7.3. Material and Methods:

In this section, effectiveness of the above mentioned process-based chlorine decay models will be evaluated for modelling chlorine decay data of single dosing scenarios. The criterion for evaluating the effectiveness of the models is considered to be the accuracy of the results the nominated models generate. That is how accurate the nominated models predict the chlorine residuals. The weighted error between experimental and model data (χ^2) can be used as a measure for assessment of the accuracy of the models.

7.3.1. Chlorine Decay Test Data

In order to compare the accuracy of the abovementioned process-based chlorine decay models, three sets of data have been considered. These three sets of data are obtained from the free chlorine decay tests undertaken by Koechling (1998) for the water samples described in Table 7.7. Tables 7.8, 7.9 and 7.10 show the chlorine decay test data obtained by Koechling (1998) for the water samples described in Table 7.7.

Table.7.7 : Water Quality Characteristics of the Water Samples from Koechling (1998)

Sample label	**Description**	**water quality characteristics**		
		DOC (mgL^{-1})	**UVA_0 (cm^{-1})**	**Alkalinity (mg/L $CaCO_3$)**
PRW	Potomac River, VA	2.80	0.100	40
QPW	Quittacas Pond, MA	4.55	0.165	5
SVR	Salt/Verde River, AZ	2.52	0.059	144

Table.7.8 : Free Chlorine Decay Test Data for Water Sample PRW (Koechling, 1998)

Time (hrs)	**Chlorine Residual (mgL^{-1})**	**Time (hrs)**	**UAV (1/cm)**
0.00	5.60	0.0	0.10031
0.10	4.86	0.1	0.07785
0.30	4.72	0.3	0.07631
0.50	4.41	0.5	0.08777
1.00	4.22	1.0	0.08505
2.00	3.94	2.0	0.07128
4.60	3.72	4.6	0.06856
8.00	2.75	8.0	0.06674
23.50	2.73	23.5	0.06104
48.00	1.86	48.0	0.05748
73.50	1.62	73.8	0.05391
125.00	1.01	125.0	0.05211

Table.7.9 : Free Chlorine Decay Test Data for Water Sample QPW (Koechling, 1998)

Time (hrs)	Chlorine Residual (mgL^{-1})	Time (hrs)	UAV (1/cm)
0.0	9.12	0.0	0.16535
0.1	7.80	0.1	0.12355
0.3	7.11	0.4	0.11762
0.5	6.63	0.5	0.11381
1.0	6.29	1.0	0.10940
2.0	5.76	2.0	0.10620
4.0	5.24	4.0	0.10144
8.0	4.57	8.0	0.09825
24.0	3.36	24.2	0.09081
48.0	2.41	48.0	0.08587
72.0	2.00	72.0	0.08237
120.0	1.17	120.0	0.07873

Table.7.10 : Free Chlorine Decay Test Data for Water Sample SVR (Koechling, 1998)

Time (hrs)	Chlorine Residual (mgL^{-1})	Time (hrs)	UAV (1/cm)
0.00	1.95	0.0	0.02364
0.10	1.33	0.1	0.01836
0.30	1.15	0.3	0.01711
0.50	1.30	0.5	0.01668
1.00	1.11	1.0	0.01645
2.00	1.02	2.0	0.01599
3.50	1.00	3.5	0.01594
4.00	0.84	4.0	0.01543
8.30	0.66	8.3	0.01488
48.50	0.50	48.5	0.01392
72.50	0.40	72.5	0.01316
120.00	0.29	120.0	0.01346

7.3.2. Data Analysis

Data analysis for chlorine decay modelling of the selected data have been performed using prepopulated Excel spreadsheets. Solver Add-in is used to undertake parameter estimation for the nominated modelling approaches. For all models, the chlorine residuals have been predicted for each data set over the entire retention time with maximum one hour intervals. The sum of squared errors (SSE) between actual and predicted data has been calculated for each data set for all models. The SSEs, which are calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy. R squared values are also calculated and compared for each set of data for all nominated models.

7.4. Results and Discussions

Table 7.11 to 7.28 show the results of chlorine decay modelling and parameter estimation for all nominated models and for the water samples PRW, QPW and SVR from Koechling (1998)'s study. The Sum Squared Errors (SSE) for the results predicted by FOM for the data set PRW with initial chlorine concentration of 5.6 mg/L is calculated to be 11.77 which appears to be the highest SSE value compared to other results. SSE values corresponding to FOM for the other two water samples of QPW and SVR are calculated to be 5.34 and 1.85, respectively. These values are also higher than the SSE values estimated for other modelling approaches. This basically confirms that FOM is the least accurate chlorine decay model. Table 7.29 compares the SSE and R squared values estimated using all nominated models for all three water samples and the ranking of each model. As can be seen from Table 7.29, MSOM and PSOM are ranked first and second amongst all nominated models. Although MSOM is ranked better than PSOM with regards to accuracy of the predicted chlorine residuals, it should be noted that MSOM contains five parameters compared to only four parameters of the PSOM and thus MSOM produces more accurate results than PSOM due to having more model parameters. Moreover, as noticed from the results, the difference in accuracy of the results between MSOM and PSOM is negligible. Since similar results for modelling any chlorine decay data set for single dosing scenario is expected, it is concluded that the PSOM is the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water for single dosing scenarios. Figures 7.1 to 7.6 show the goodness of data fitting of chlorine decay modelling using the nominated models for all selected chlorine decay data sets.

Table.7.11 : Comparison of Chlorine Decay Modelling Results using FOM for PRW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		FOM	
Data Set Name:		PRW (RAW) Water Sample; Koechling (1998)	
Model Parameter		k	0.034
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	5.60	5.60	0.00
0.10	4.86	5.58	0.52
0.30	4.72	5.54	0.68
0.50	4.41	5.51	1.20
1.00	4.22	5.41	1.43
2.00	3.94	5.24	1.68
4.60	3.72	4.80	1.16
8.00	2.75	4.28	2.33
23.50	2.73	2.54	0.04
48.00	1.86	1.11	0.56
73.50	1.62	0.47	1.32
125.00	1.01	0.08	0.86
		Sum Squared Error (SSE)	11.77
		R Squared (R^2)	0.8861

Table.7.12 : Comparison of Chlorine Decay Modelling Results using FOM for QPW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		FOM	
Data Set Name:		QPW (RAW) Water Sample; Koechling (1998)	
Model Parameter		k	0.032
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	3.40	3.40	0.00
0.10	2.93	3.39	0.21
0.30	2.67	3.37	0.49
0.50	2.56	3.35	0.62
1.00	2.44	3.29	0.73
2.00	2.27	3.19	0.85
4.00	2.11	3.00	0.79
8.30	1.89	2.62	0.53
24.00	1.53	1.59	0.00
50.00	1.20	0.70	0.25
74.00	1.00	0.33	0.45
121.00	0.73	0.07	0.43
		Sum Squared Error (SSE)	5.34
		R Squared (R^2)	0.8688

Table.7.13 : Comparison of Chlorine Decay Modelling Results using FOM for SVR Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		FOM	
Data Set Name:		SVR (RAW) Water Sample; Koechling (1998)	
Model Parameter		k	0.255
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	1.95	1.95	0.00
0.10	1.33	1.90	0.33
0.30	1.15	1.81	0.43
0.50	1.30	1.72	0.17
1.00	1.11	1.51	0.16
2.00	1.02	1.17	0.02
3.50	1.00	0.80	0.04
4.00	0.84	0.70	0.02
8.30	0.66	0.23	0.18
48.50	0.50	0.00	0.25
72.50	0.40	0.00	0.16
120.00	0.29	0.00	0.08
		Sum Squared Error (SSE)	1.85
		R Squared (R^2)	0.8404

Table.7.14 : Comparison of Chlorine Decay Modelling Results using PFOM for PRW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		PFOM	
Data Set Name:		PRW (RAW) Water Sample; Koechling (1998)	
Model Parameters		k_FRA	1.709
		k_SRA	0.012
		f	0.345
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	5.60	5.60	0.00
0.10	4.86	5.29	0.19
0.30	4.72	4.81	0.01
0.50	4.41	4.47	0.00
1.00	4.22	3.97	0.06
2.00	3.94	3.64	0.09
4.60	3.72	3.47	0.06
8.00	2.75	3.33	0.34
23.50	2.73	2.77	0.00
48.00	1.86	2.06	0.04
73.50	1.62	1.52	0.01
125.00	1.01	0.82	0.04
		Sum Squared Error (SSE)	0.84
		R Squared (R^2)	0.9660

Table.7.15 : Comparison of Chlorine Decay Modelling Results using PFOM for QPW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		PFOM	
Data Set Name:		QPW (RAW) Water Sample; Koechling (1998)	
Model Parameters		k_FRA	0.011
		k_SRA	2.805
		f	0.651
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	3.40	3.40	0.00
0.10	2.93	3.11	0.03
0.30	2.67	2.72	0.00
0.50	2.56	2.49	0.00
1.00	2.44	2.26	0.03
2.00	2.27	2.17	0.01
4.00	2.11	2.12	0.00
8.30	1.89	2.02	0.02
24.00	1.53	1.70	0.03
50.00	1.20	1.27	0.00
74.00	1.00	0.97	0.00
121.00	0.73	0.58	0.02
		Sum Squared Error (SSE)	0.15
		R Squared (R^2)	0.9804

Table.7.16 : Comparison of Chlorine Decay Modelling Results using PFOM for SVR Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		PFOM	
Data Set Name:		SVR (RAW) Water Sample; Koechling (1998)	
Model Parameters		k_FRA	9.922
		k_SRA	0.014
		f	0.463
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	1.95	1.95	0.00
0.10	1.33	1.38	0.00
0.30	1.15	1.09	0.00
0.50	1.30	1.05	0.06
1.00	1.11	1.03	0.01
2.00	1.02	1.02	0.00
3.50	1.00	1.00	0.00
4.00	0.84	0.99	0.02
8.30	0.66	0.93	0.07
48.50	0.50	0.52	0.00
72.50	0.40	0.37	0.00
120.00	0.29	0.19	0.01
		Sum Squared Error (SSE)	0.18
		R Squared (R^2)	0.9235

Table.7.17 : Comparison of Chlorine Decay Modelling Results using MPFOM for PRW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MPFOM	
Data Set Name:		PRW (RAW) Water Sample; Koechling (1998)	
Model Parameters		FRA0	1.682
		SRA0	2.895
		k_FRA	2.431
		k_SRA	0.026
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	5.60	5.60	0.00
0.10	4.86	5.23	0.14
0.30	4.72	4.71	0.00
0.50	4.41	4.38	0.00
1.00	4.22	3.99	0.05
2.00	3.94	3.78	0.02
4.60	3.72	3.59	0.02
8.00	2.75	3.37	0.39
23.50	2.73	2.59	0.02
48.00	1.86	1.85	0.00
73.50	1.62	1.45	0.03
125.00	1.01	1.13	0.02
		Sum Squared Error (SSE)	0.68
		R Squared (R^2)	0.9709

Table.7.18 : Comparison of Chlorine Decay Modelling Results using MPFOM for QPW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MPFOM	
Data Set Name:		QPW (RAW) Water Sample; Koechling (1998)	
Model Parameters		FRA0	1.045
		SRA0	1.598
		k_FRA	3.922
		k_SRA	0.029
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	3.40	3.40	0.00
0.10	2.93	3.06	0.02
0.30	2.67	2.66	0.00
0.50	2.56	2.48	0.01
1.00	2.44	2.33	0.01
2.00	2.27	2.26	0.00
4.00	2.11	2.18	0.00
8.30	1.89	2.01	0.01
24.00	1.53	1.55	0.00
50.00	1.20	1.13	0.01
74.00	1.00	0.94	0.00
121.00	0.73	0.80	0.01
		Sum Squared Error (SSE)	0.07
		R Squared (R^2)	0.9908

Table.7.19 : Comparison of Chlorine Decay Modelling Results using MPFOM for SVR Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MPFOM	
Data Set Name:		SVR (RAW) Water Sample; Koechling (1998)	
Model Parameters		FRA0	0.751
		SRA0	0.807
		k_FRA	10.000
		k_SRA	0.120
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	1.95	1.95	0.00
0.10	1.33	1.47	0.02
0.30	1.15	1.21	0.00
0.50	1.30	1.16	0.02
1.00	1.11	1.11	0.00
2.00	1.02	1.03	0.00
3.50	1.00	0.92	0.01
4.00	0.84	0.89	0.00
8.30	0.66	0.69	0.00
48.50	0.50	0.40	0.01
72.50	0.40	0.39	0.00
120.00	0.29	0.39	0.01
		Sum Squared Error (SSE)	0.07
		R Squared (R^2)	0.9696

Table.7.20 : Comparison of Chlorine Decay Modelling Results using SOM for PRW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		SOM	
Data Set Name:		PRW (RAW) Water Sample; Koechling (1998)	
Model Parameters		RA_0	3.855
		k	0.053
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	5.60	5.60	0.00
0.10	4.86	5.49	0.40
0.30	4.72	5.28	0.32
0.50	4.41	5.10	0.47
1.00	4.22	4.69	0.22
2.00	3.94	4.09	0.02
4.60	3.72	3.18	0.29
8.00	2.75	2.61	0.02
23.50	2.73	1.90	0.70
48.00	1.86	1.76	0.01
73.50	1.62	1.75	0.02
125.00	1.01	1.75	0.54
		Sum Squared Error (SSE)	3.00
		R Squared (R^2)	0.9062

Table.7.21 : Comparison of Chlorine Decay Modelling Results using SOM for QPW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		SOM	
Data Set Name:		QPW (RAW) Water Sample; Koechling (1998)	
Model Parameters		RA_0	2.208
		k	0.139
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	3.40	3.40	0.00
0.10	2.93	3.30	0.14
0.30	2.67	3.12	0.20
0.50	2.56	2.96	0.16
1.00	2.44	2.65	0.05
2.00	2.27	2.24	0.00
4.00	2.11	1.79	0.10
8.30	1.89	1.43	0.21
24.00	1.53	1.21	0.10
50.00	1.20	1.19	0.00
74.00	1.00	1.19	0.04
121.00	0.73	1.19	0.21
		Sum Squared Error (SSE)	1.22
		R Squared (R^2)	0.8748

Table.7.22 : Comparison of Chlorine Decay Modelling Results using SOM for SVR Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		SOM	
Data Set Name:		SVR (RAW) Water Sample; Koechling (1998)	
Model Parameters		RA_0	1.379
		k	0.801
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	1.95	1.95	0.00
0.10	1.33	1.76	0.18
0.30	1.15	1.49	0.11
0.50	1.30	1.31	0.00
1.00	1.11	1.03	0.01
2.00	1.02	0.80	0.05
3.50	1.00	0.67	0.11
4.00	0.84	0.64	0.04
8.30	0.66	0.58	0.01
48.50	0.50	0.57	0.01
72.50	0.40	0.57	0.03
120.00	0.29	0.57	0.08
		Sum Squared Error (SSE)	0.63
		R Squared (R^2)	0.7839

Table.7.23 : Comparison of Chlorine Decay Modelling Results using MSOM for PRW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MSOM	
Data Set Name:		PRW (RAW) Water Sample; Koechling (1998)	
Model Parameters		FRA0	1.838
		k_FRA	2.060
		SRA0	3.502
		k_SRA	0.007
		Z	0.312
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	5.60	5.60	0.00
0.10	4.86	5.11	0.06
0.30	4.72	4.63	0.01
0.50	4.41	4.39	0.00
1.00	4.22	4.10	0.01
2.00	3.94	3.86	0.01
4.60	3.72	3.55	0.03
8.00	2.75	3.28	0.28
23.50	2.73	2.53	0.04
48.00	1.86	1.88	0.00
73.50	1.62	1.51	0.01
125.00	1.01	1.10	0.01
		Sum Squared Error (SSE)	0.47
		R Squared (R^2)	0.9797

Table.7.24 : Comparison of Chlorine Decay Modelling Results using MSOM for QPW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MSOM	
Data Set Name:		QPW (RAW) Water Sample; Koechling (1998)	
Model Parameters		FRA0	1.148
		k_FRA	5.138
		SRA0	1.866
		k_SRA	0.012
		Z	0.328
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	3.40	3.40	0.00
0.10	2.93	2.98	0.00
0.30	2.67	2.67	0.00
0.50	2.56	2.53	0.00
1.00	2.44	2.39	0.00
2.00	2.27	2.26	0.00
4.00	2.11	2.14	0.00
8.30	1.89	1.95	0.00
24.00	1.53	1.53	0.00
50.00	1.20	1.16	0.00
74.00	1.00	0.97	0.00
121.00	0.73	0.76	0.00
		Sum Squared Error (SSE)	0.01
		R Squared (R^2)	0.9981

Table.7.25 : Comparison of Chlorine Decay Modelling Results using MSOM for SVR Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		MSOM	
Data Set Name:		SVR (RAW) Water Sample; Koechling (1998)	
Model Parameters		FRA0	0.806
		k_FRA	10.000
		SRA0	0.959
		k_SRA	0.117
		Z	0.593
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)	Squared Error
0.00	1.95	1.95	0.00
0.10	1.33	1.47	0.02
0.30	1.15	1.23	0.01
0.50	1.30	1.15	0.02
1.00	1.11	1.07	0.00
2.00	1.02	1.00	0.00
3.50	1.00	0.92	0.01
4.00	0.84	0.89	0.00
8.30	0.66	0.75	0.01
48.50	0.50	0.43	0.00
72.50	0.40	0.39	0.00
120.00	0.29	0.37	0.01
		Sum Squared Error (SSE)	0.08
		R Squared (R^2)	0.9669

Table.7.26 : Comparison of Chlorine Decay Modelling Results using PSOM for PRW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		PSOM		
Data Set Name:		PRW (RAW) Water Sample; Koechling (1998)		
Model Parameters		FRA0		1.488
		SRA0		3.362
		k_FRA		0.645
		k_SRA		0.009
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)		Squared Error
		Cl_FRA(t)	Cl(t)	
0.00	5.60	5.60	5.60	0.00
0.10	4.86	5.16	5.15	0.08
0.30	4.72	4.67	4.63	0.01
0.50	4.41	4.42	4.36	0.00
1.00	4.22	4.19	4.07	0.02
2.00	3.94	4.12	3.88	0.00
4.60	3.72	4.11	3.61	0.01
8.00	2.75	4.11	3.32	0.33
23.50	2.73	4.11	2.48	0.06
48.00	1.86	4.11	1.83	0.00
73.50	1.62	4.11	1.49	0.02
125.00	1.01	4.11	1.15	0.02
		Sum Squared Error (SSE)		0.57
		R Squared (R^2)		0.9756

Table.7.27 : Comparison of Chlorine Decay Modelling Results using PSOM for QPW Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		PSOM		
Data Set Name:		QPW (RAW) Water Sample; Koechling (1998)		
Model Parameters		FRA0		0.994
		SRA0		1.831
		k_FRA		1.470
		k_SRA		0.015
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)		Squared Error
		Cl_FRA(t)	Cl(t)	
0.00	3.40	3.40	3.40	0.00
0.10	2.93	3.03	3.02	0.01
0.30	2.67	2.68	2.66	0.00
0.50	2.56	2.53	2.50	0.00
1.00	2.44	2.43	2.36	0.01
2.00	2.27	2.41	2.28	0.00
4.00	2.11	2.41	2.17	0.00
8.30	1.89	2.41	1.97	0.01
24.00	1.53	2.41	1.51	0.00
50.00	1.20	2.41	1.14	0.00
74.00	1.00	2.41	0.96	0.00
121.00	0.73	2.41	0.79	0.00
		Sum Squared Error (SSE)		0.04
		R Squared (R^2)		0.9949

Table.7.28 : Comparison of Chlorine Decay Modelling Results using PSOM for SVR Data Set (Single Chlorine Dosing)

Chlorine Decay Model Name:		PSOM		
Data Set Name:		SVR (RAW) Water Sample; Koechling (1998)		
Model Parameters		FRA0		0.706
		SRA0		0.872
		k_FRA		10.000
		k_SRA		0.124
time	Measured Chlorine Concentration (mg/L)	Predicted Chlorine Concentration Cl(t) (mg/L)		Squared Error
		Cl_FRA(t)	Cl(t)	
0.00	1.95	1.95	1.95	0.00
0.10	1.33	1.39	1.37	0.00
0.30	1.15	1.25	1.22	0.00
0.50	1.30	1.24	1.18	0.01
1.00	1.11	1.24	1.12	0.00
2.00	1.02	1.24	1.03	0.00
3.50	1.00	1.24	0.92	0.01
4.00	0.84	1.24	0.89	0.00
8.30	0.66	1.24	0.71	0.00
48.50	0.50	1.24	0.40	0.01
72.50	0.40	1.24	0.38	0.00
120.00	0.29	1.24	0.37	0.01
		Sum Squared Error (SSE)		0.05
		R Squared (R^2)		0.9794

Table.7.29 : Comparison of SSE and R^2 Values for all Nominated Models for Water Samples PRW, QPW and SVR (Single Chlorine Dosing)

Chlorine Decay Model Name	Data Set Name						
	PRW		QPW		SVR		
	Sum Squared Error (SSE)	R Squared (R2)	Sum Squared Error (SSE)	R Squared (R2)	Sum Squared Error (SSE)	R Squared (R2)	
FOM	11.77	0.8861	5.34	0.8688	1.85	0.8404	6
PFOM	0.84	0.9660	0.15	0.9804	0.18	0.9235	4
MPFOM	0.68	0.9709	0.07	0.9908	0.07	0.9696	3
SOM	3.00	0.9062	1.22	0.8748	0.63	0.7839	5
MSOM	0.47	0.9797	0.01	0.9981	0.08	0.9669	1
PSOM	0.57	0.9756	0.04	0.9949	0.05	0.9794	2

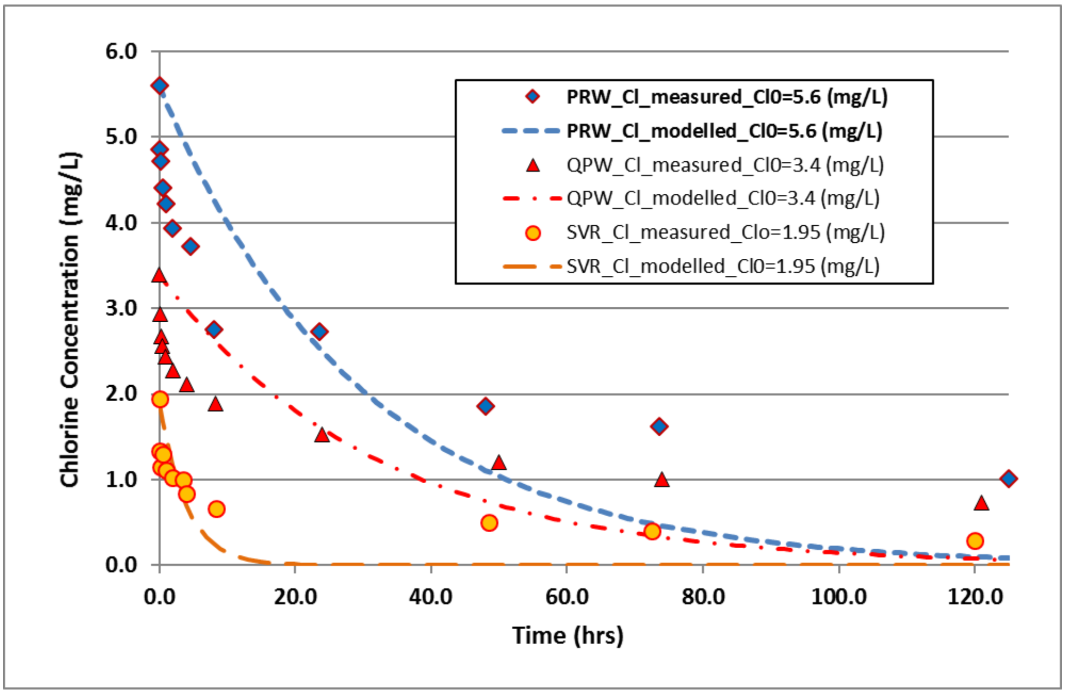


Fig.7.1.Goodness of data fitting of chlorine decay modelling using FOM for water samples PRW, QPW and SVR from Koechling (1998)'s study

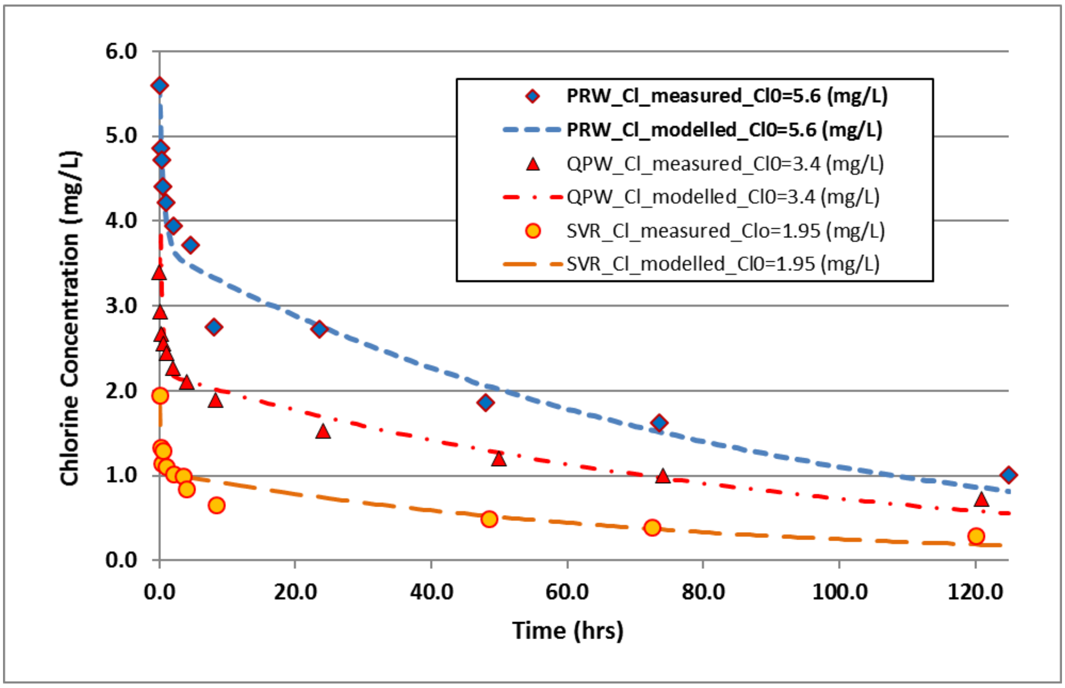


Fig.7.2. Goodness of data fitting of chlorine decay modelling using PFOM for water samples PRW, QPW and SVR from Koechling (1998)'s study

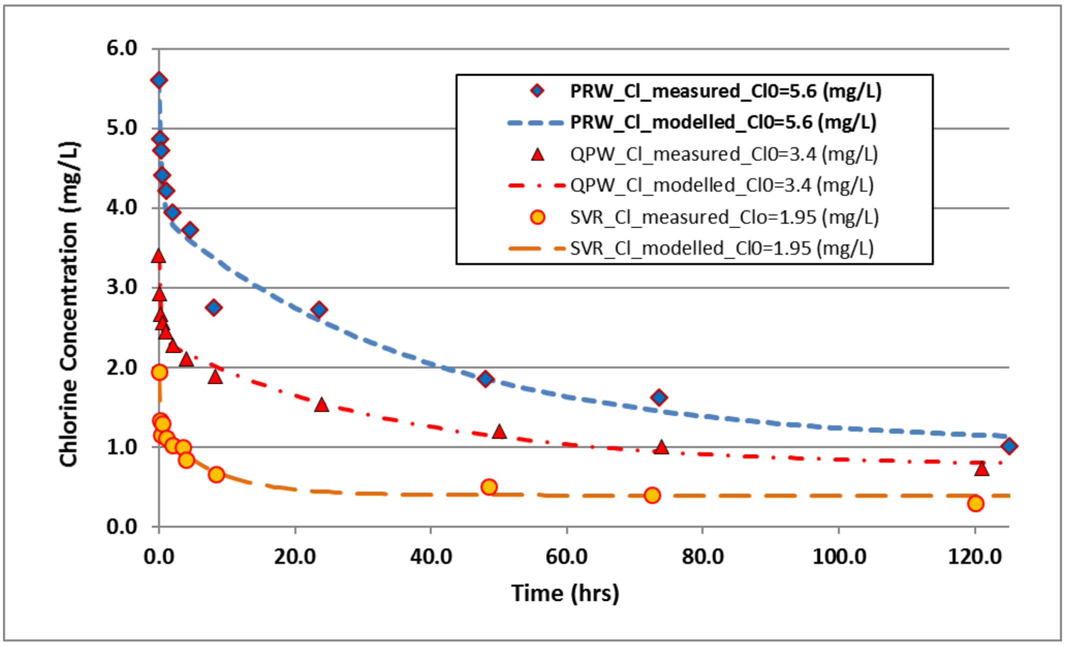


Fig.7.3. Goodness of data fitting of chlorine decay modelling using MPFOM for water samples PRW, QPW and SVR from Koechling (1998)'s study

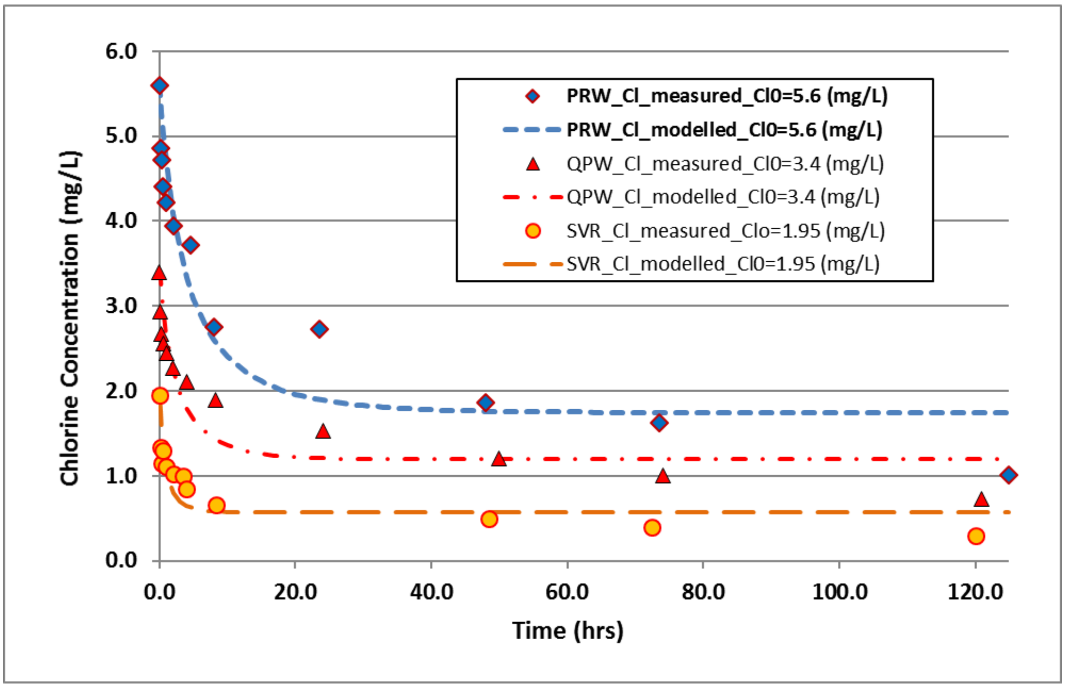


Fig.7.4.Goodness of data fitting of chlorine decay modelling using SOM for water samples PRW, QPW and SVR from Koechling (1998)'s study

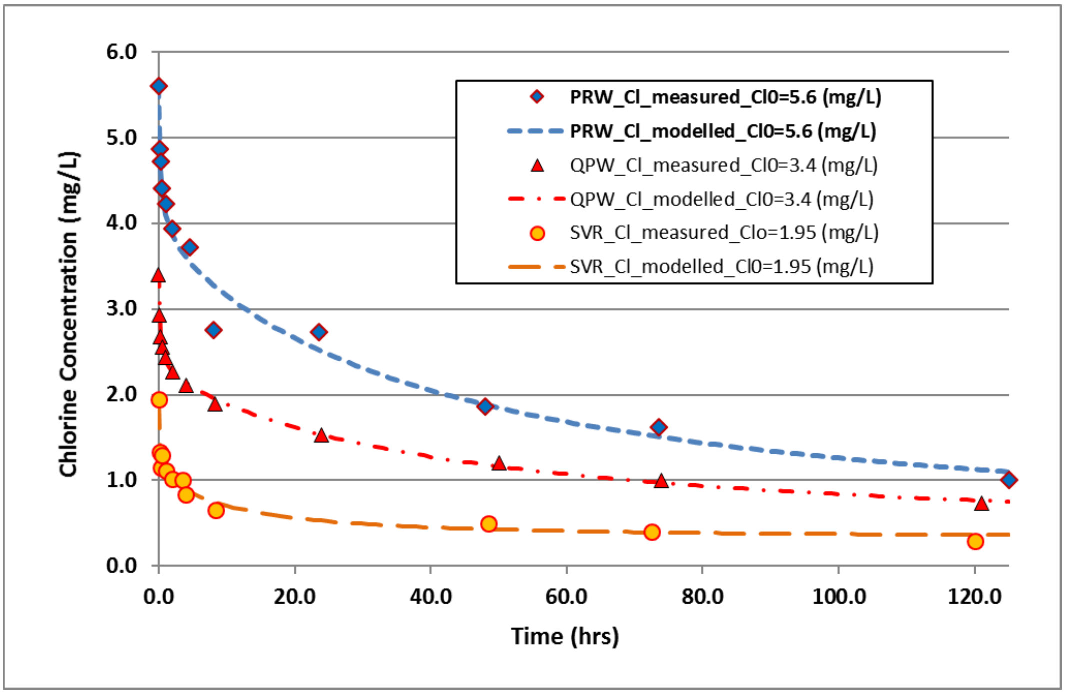


Fig.7.5.Goodness of data fitting of chlorine decay modelling using MSOM for water samples PRW, QPW and SVR from Koechling (1998)'s study

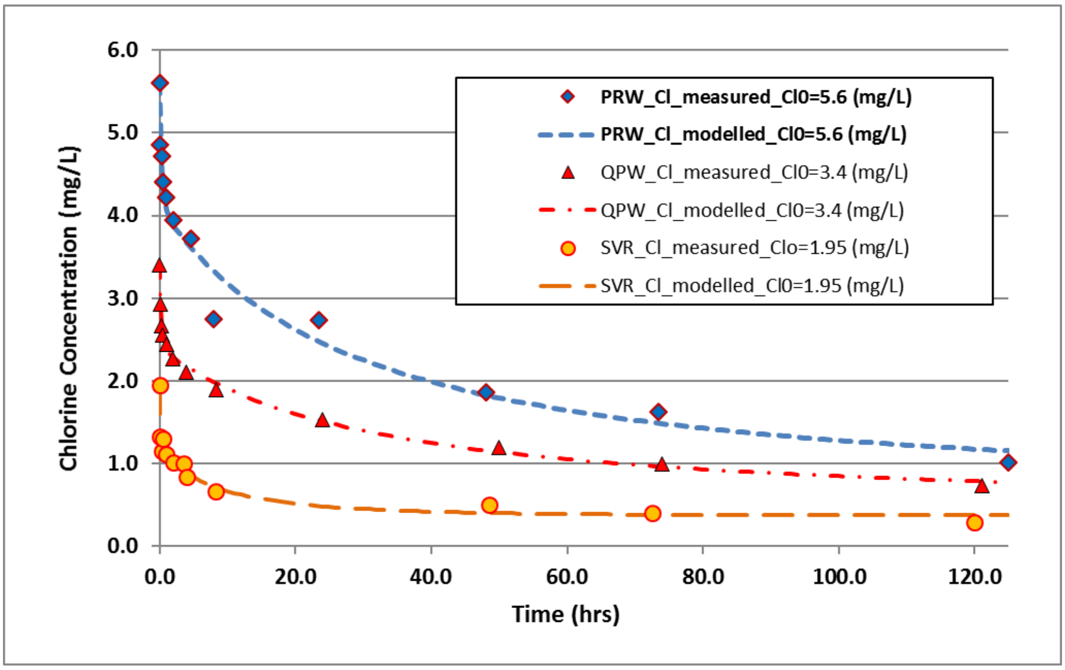


Fig.7.6.Goodness of data fitting of chlorine decay modelling using PSOM for water samples PRW, QPW and SVR from Koechling (1998)'s study

7.5. Conclusion

In this chapter, four already well known process-based chlorine decay models as well as two new models were evaluated for the accuracy of their results for single dosing scenario. The nominated models are First Order Model (FOM), Parallel First Order Model (PFOM), Modified Parallel First Order Model (MPFOM), Second Order Model (SOM), Modified Second Order Model (MSOM) and Parallel Second Order Model (PSOM).

Accuracy of the abovementioned process-based chlorine decay models was analysed using three sets of chlorine decay data. The chlorine decay data was obtained from the free chlorine decay tests undertaken by Koechling (1998).

Data analysis for chlorine decay modelling of the selected data was performed using prepopulated Excel spreadsheets. Solver Add-in was used to undertake parameter estimation for the nominated modelling approaches. The sum of squared errors (SSE) between actual and predicted data was calculated for each data set for all models. The SSEs, which are calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy.

The models were ranked based on the results of their SSE values. Lower the SSE of the model was, the higher the model was ranked. MSOM and PSOM were ranked first and second amongst all nominated models. Although MSOM was ranked better than PSOM with regards to accuracy of the predicted chlorine residuals, it should be noted that MSOM contained five parameters compared to only four parameters of the PSOM and thus MSOM produced more accurate results than PSOM due to having more model parameters. Also, it was noticed that the difference in accuracy of the results between MSOM and PSOM was negligible. Therefore, it was concluded that the PSOM was the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water for single dosing scenarios.

8. Comparison of the Accuracy of the Process-Based Chlorine Decay Models for Multiple Dosing Scenario

8.1. Introduction

One of the most important requirements for chlorine decay models is the ability of the models to accurately represent the multiple dosing scenarios. As discussed earlier, primary chlorination usually occurs at the end of water treatment process where treated water enters distribution system. The initial chlorine concentration during chlorination, however, may not be accurately known. One of the reasons for not knowing the initial chlorine concentration is that water quality characteristics and therefore initial chlorine demand and CT values may change during treatment process. Another reason may be the need for temporarily increasing the chlorine dose due to maintenance requirements. Also, initial chlorine doses may need to be changed due to temperature variation or due to altering water treatment processes. Consequently, it is important for chlorine decay model to be able to predict the chlorine residuals at various locations of the water distribution system with changing chlorine doses. In order to test a chlorine decay model against this criterion, accuracy of the model in predicting the chlorine residuals in bulk water for multiple chlorine dosing scenario needs to be evaluated.

In this chapter, the previously discussed process-based chlorine decay models will be evaluated for the accuracy of their results for multiple dosing scenario. In order to compare the accuracy of different models the weighted error (sum of errors or chi^2- chi squared) between experimental and model data (χ^2) can be used as a measure of accuracy of a chlorine decay model. The weighted error (sum of errors or chi^2- chi squared) can be defined as follows:

$$\chi^2(p) = \sum_{i=1}^{n} \left(\frac{f_{meas\_i} - f_i(p)}{\sigma_{meas\_i}}\right)^2 \qquad (9.1)$$

where f_{meas_i} is the ith measured value, $f_i(p)$ is the calculated value from the model using parameter values p and σ_{meas_i} is the estimated standard deviation of f_{meas_i}.

8.2. Material and Methods:

Two different sets of chlorine decay data will be used for the accuracy assessment of the six nominated process-based chlorine decay models. One set of data was acquired by undertaking chlorine decay tests on water sample taken from Harding Dam Water

Treatment Plant in Pilbara region. Another set of chlorine decay data was selected from independent data existing in the literature.

8.2.1. Pilbara Water Sample Chlorine Decay Test Results

One of the water samples taken from post filtration section at Pilbara Water Treatment Plant was used for chlorine decay test for this research. The water sample was labelled as PPFW. Table 8.1 shows water quality characteristics of the samples obtained taken from Pilbara treatment plant.

Table.8.1 : Water Quality Characteristics for the PPFW Sample

Sample label	**Description**	**water quality characteristics**		
		DOC (mg/L)	**UV254**	**pH**
PPFW	Pilbara Post-Filtration Water	2.16	0.022	7.65

Water samples were stored in the prepared chlorine-demand-free amber bottles. N,N-diethyl-p-phenylenediamine (DPD) colorimetric method was used to conduct chlorine measurements using Lovibond® pocket colorimeter. Repeated tests were undertaken for each experiment to minimise the effects of variations in the water quality and also to reduce the impact from potential human errors. The test results were compared for consistency. For chlorination of the samples, diluted standard sodium hypochlorite solution was used. In order to confirm the initial chlorine concentration (initial dose), several experiments with de-ionized water were conducted before undertaking the main tests. Prepared chlorine-demand-free plastic bottles were used to store the water samples. Temperature condition of the samples was maintained constant by keeping the samples inside the water bath. Before starting any sampling for the experiments, all containers and glassware were cleaned with de-ionized water to ensure that no chlorine demand was present. Duplicate analysis was performed on each sample to get an accuracy of ±0.05 mg/L, and the average was reported.

The chlorine decay tests for PPFW sample were conducted for three initial chlorine concentrations (3.2 mg/L, 5.4 mg/L and 8.4 mg/L) at 25˚C. Tables 8.2 shows the free chlorine decay test data for the PPFW sample.

Table.8.2 : Free Chlorine Decay Test Data for PPFW Sample (25˚C)

Time (hrs)	**Initial Chlorine Concentration (Dose) (mgL^{-1})**		
	3.2	**5.4**	**8.4**
	Chlorine Residual (mgL^{-1})		
0	3.20	5.40	8.40
0.08	2.60	4.59	7.62
0.17	2.54	4.57	7.88
0.33	2.43	4.65	7.38
0.67	2.41	4.44	7.46
1	2.27	4.25	7.36
2	2.10	4.13	6.86
4	1.87	3.82	6.40
6	1.75	3.53	6.00
8	1.65	3.49	5.84
10	1.54	3.41	5.80
24	1.20	2.92	5.28
48	0.74	2.53	4.71
72	0.45	2.24	4.31
96	0.25	1.98	3.89
120	0.16	1.60	3.53
144	0.05	1.35	3.16
168	0.00	1.15	2.97
192	0.00	0.97	2.85
240	0.00	0.59	2.39

8.2.2. Selection of Literature (Independent) Data

The literature data is extracted from the research work performed by Warton et al. (2006). In their research, a sample of groundwater taken from an artesian aquifer near Wanneroo groundwater treatment plant (GWTP), Perth, Western Australia, was dosed with chlorine at various concentrations of 4, 6, 8 and 10 mg/L and residual chlorine concentrations were measured periodically over a period of 168 hours. Table 8.3 presents the water quality characteristics of the water sample used in Warton et al. (2006)'s research. Table 8.4 shows the free chlorine decay test data for this sample.

Table.8.3 : Water Quality Characteristics of the Water Sample Used in Warton et al. (2006)'s Research Study

Reference	Sample label	Description	Water quality characteristics			
			DOC (mgL^{-1})	UV254 (cm^{-1})	pH	Alkalinity (mgL^{-1} CaCO3)
Warton et al. (2006)	ABW257	Artesian Bore W257	1.8	0.058	7.97	95

Table.8.4 : Free Chlorine Decay Test Data for the Water Sample Used in Warton et al. (2006)'s Research Study

Time (hrs)	Initial Chlorine Concentration (Dose) (mgL^{-1})			
	4.0	6.0	8.0	10.0
	Chlorine Residual (mgL^{-1})			
0	4.00	6	8	10
0.08	3.25	4.68	6.42	8.09
0.25	2.39	4.05	5.86	7.79
0.5	2.00	3.9	5.78	7.69
1	1.85	3.87	5.69	7.59
1.5	1.78	3.79	5.58	7.59
2	1.70	3.76	5.58	7.54
2.5	1.70	3.6	5.58	7.44
3	1.67	3.6	5.54	7.44
3.5	1.60	3.58	5.5	7.4
4	1.58	3.54	5.41	7.28
21	1.04	3.09	5.06	6.75
30	1.00	3.02	4.98	6.55
50	0.84	2.84	4.66	6.04
72	0.53	2.38	4.17	5.54
96	0.42	2.3	4.17	5.49
101	0.33	2.27	4.01	5.34
120	0.26	2.12	4.01	5.29
144	0.14	1.99	3.89	5.14
168	0.11	1.87	3.77	4.88

8.2.3. Data Analysis

Data analysis for chlorine decay modelling of the selected data has been performed using prepopulated Excel spreadsheets. Solver Add-in is used to undertake parameter estimation for the nominated modelling approaches. For all models, the chlorine residuals have been predicted for each data set over the entire retention time with maximum one hour intervals. The sum of squared errors (SSE) between actual and predicted data has been calculated for each data set for all models. The SSEs, which are calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy. R squared values are also calculated and compared for each set of data for all nominated models.

8.3. Results and Discussions

Tables 8.5 to 8.10 show the results of chlorine decay modelling and parameter estimation for all nominated models and for the water sample PPFW from Pilbara Post- Filtration Water Treatment Plant. The Sum Squared Errors (SSE) for the results predicted by FOM for this data set with various initial chlorine concentrations of 3.2, 5.4 and 8.4 mg/L is calculated to be 65.14 which appears to be the highest SSE value compared to other results. SSE values corresponding to PFOM, MPFOM, SOM, MSOM and PSOM for the same water sample are calculated to be 16.02, 9.99, 19.20, 2.91 and 3.60, respectively.

Similarly, Tables 8.11 to 8.16 show the results of chlorine decay modelling and parameter estimation for all nominated models and for the water sample that is extracted from the research work performed by Warton et al. (2006). The Sum Squared Errors (SSE) for the results predicted by FOM for this data set with various initial chlorine concentrations of 4, 6, 8 and 10 mg/L is calculated to be 248.51 which appears to be the highest SSE value compared to other results. SSE values corresponding to PFOM, MPFOM, SOM, MSOM and PSOM for the same water sample are calculated to be 43.48, 5.59, 36.45, 1.70 and 3.44, respectively.

One of the reasons that PFOM and PSOM generate more accurate results compared to FOM and SOM is that the parallel first and second order models (PFOM and PSOM) contain more parameters that need to be estimated and therefore that have more flexibility to fit the data.

Table 8.11 compares the SSE and R^2 values estimated using all nominated chlorine decay models for the selected water samples and the ranking of each model. Also, Figure 8.13 presents the SSE values graphically for all models and the selected water samples. Figure 8.14 shows the R^2 values calculated for all nominated chlorine decay models. As can be seen from Table 8.11 and Figure 8.13 MSOM and PSOM are ranked first and second amongst all nominated models. Although MSOM is ranked better than PSOM with regards to accuracy of the predicted chlorine residuals, it should be noted that MSOM contains five parameters compared to only four parameters of the PSOM and thus it can be said that MSOM produces more accurate results than PSOM due to having more model parameters. Moreover, as noticed from the results, the difference in accuracy of the results between MSOM and PSOM is negligible. Therefore, it is concluded that the PSOM is the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water for multiple dosing scenarios. Figures 8.1 to 8.12 show the goodness of data fitting of chlorine decay modelling using the nominated models for all selected chlorine decay data sets.

Table.8.5 : Comparison of Chlorine Decay Modelling Results using FOM for PPFW Data Set (Multiple Chlorine Dosing)

Chlorine Decay Model Name:				FOM			
Data Set Name:				Pilbara Water Sample (PPFW)			
Model Parameters					k		0.010
time (hr)	Measured Chlorine Concentration (mg/L)			Predicted Chlorine Concentration Cl(t) (mg/L)			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	2.60	4.59	7.62	3.20	5.40	8.39	1.60
0.17	2.54	4.57	7.88	3.19	5.39	8.39	1.36
0.33	2.43	4.65	7.38	3.19	5.38	8.37	2.10
0.67	2.41	4.44	7.46	3.18	5.36	8.34	2.22
1.00	2.27	4.25	7.36	3.17	5.34	8.31	2.91
2.00	2.10	4.13	6.86	3.14	5.29	8.23	4.29
4.00	1.87	3.82	6.40	3.07	5.18	8.06	6.07
6.00	1.75	3.53	6.00	3.01	5.08	7.90	7.59
8.00	1.65	3.49	5.84	2.95	4.97	7.74	7.49
10.00	1.54	3.41	5.80	2.89	4.87	7.58	7.13
24.00	1.20	2.92	5.28	2.50	4.22	6.57	5.05
48.00	0.74	2.53	4.71	1.96	3.30	5.14	2.26
72.00	0.45	2.24	4.31	1.53	2.58	4.02	1.37
96.00	0.25	1.98	3.89	1.20	2.02	3.14	1.46
120.00	0.16	1.60	3.53	0.94	1.58	2.45	1.76
144.00	0.05	1.35	3.16	0.73	1.23	1.92	2.02
168.00	0.00	1.15	2.97	0.57	0.96	1.50	2.52
192.00	0.00	0.97	2.85	0.45	0.75	1.17	3.06
240.00	0.00	0.59	2.39	0.27	0.46	0.72	2.89
Sum Squared Error (SSE)							65.14
R Squared (R2)							0.9116

Table.8.6 : Comparison of Chlorine Decay Modelling Results using PFOM for PPFW Data Set (Multiple Chlorine Dosing)

Chlorine Decay Model Name:				PFOM			
Data Set Name:				Pilbara Water Sample (PPFW)			
Model Parameters				k_FRA			0.946
				k_SRA			0.006
				f			0.299
time (hr)	Measured Chlorine Concentration (mg/L)			Predicted Chlorine Concentration Cl(t) (mg/L)			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	2.60	4.59	7.62	3.13	5.28	8.21	1.11
0.17	2.54	4.57	7.88	3.06	5.16	8.02	0.63
0.33	2.43	4.65	7.38	2.94	4.96	7.72	0.47
0.67	2.41	4.44	7.46	2.74	4.63	7.20	0.21
1.00	2.27	4.25	7.36	2.60	4.39	6.83	0.41
2.00	2.10	4.13	6.86	2.36	3.99	6.20	0.53
4.00	1.87	3.82	6.40	2.21	3.74	5.81	0.47
6.00	1.75	3.53	6.00	2.17	3.67	5.70	0.29
8.00	1.65	3.49	5.84	2.15	3.62	5.63	0.31
10.00	1.54	3.41	5.80	2.12	3.58	5.57	0.42
24.00	1.20	2.92	5.28	1.96	3.31	5.15	0.75
48.00	0.74	2.53	4.71	1.72	2.90	4.51	1.13
72.00	0.45	2.24	4.31	1.50	2.54	3.95	1.33
96.00	0.25	1.98	3.89	1.32	2.22	3.45	1.38
120.00	0.16	1.60	3.53	1.15	1.94	3.02	1.36
144.00	0.05	1.35	3.16	1.01	1.70	2.64	1.31
168.00	0.00	1.15	2.97	0.88	1.49	2.31	1.32
192.00	0.00	0.97	2.85	0.77	1.30	2.03	1.39
240.00	0.00	0.59	2.39	0.59	1.00	1.55	1.22
Sum Squared Error (SSE)							16.02
R Squared (R^2)							0.9754

Table.8.7 : Comparison of Chlorine Decay Modelling Results using MPFOM for PPFW Data Set (Multiple Chlorine Dosing)

Chlorine Decay Model Name:				MPFOM			
Data Set Name:				Pilbara Water Sample (PPFW)			
Model Parameters				FRA0			1.552
				SRA0			4.176
				k_FRA			1.669
				k_SRA			0.009
time (hr)	Measured Chlorine Concentration (mg/L)			Predicted Chlorine Concentration Cl(t) (mg/L)			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	2.60	4.59	7.62	3.00	5.20	8.20	0.88
0.17	2.54	4.57	7.88	2.81	5.01	8.01	0.28
0.33	2.43	4.65	7.38	2.53	4.73	7.73	0.14
0.67	2.41	4.44	7.46	2.13	4.33	7.33	0.11
1.00	2.27	4.25	7.36	1.90	4.10	7.10	0.23
2.00	2.10	4.13	6.86	1.62	3.82	6.82	0.32
4.00	1.87	3.82	6.40	1.50	3.70	6.70	0.24
6.00	1.75	3.53	6.00	1.42	3.62	6.62	0.50
8.00	1.65	3.49	5.84	1.34	3.54	6.54	0.59
10.00	1.54	3.41	5.80	1.27	3.47	6.47	0.53
24.00	1.20	2.92	5.28	0.80	3.00	6.00	0.69
48.00	0.74	2.53	4.71	0.13	2.33	5.33	0.80
72.00	0.45	2.24	4.31	0.00	1.79	4.79	0.64
96.00	0.25	1.98	3.89	0.00	1.36	4.36	0.67
120.00	0.16	1.60	3.53	0.00	1.02	4.02	0.60
144.00	0.05	1.35	3.16	0.00	0.75	3.75	0.71
168.00	0.00	1.15	2.97	0.00	0.53	3.53	0.70
192.00	0.00	0.97	2.85	0.00	0.36	3.36	0.63
240.00	0.00	0.59	2.39	0.00	0.11	3.11	0.75
Sum Squared Error (SSE)							9.99
R Squared (R^2)							0.9715

Table.8.8 : Comparison of Chlorine Decay Modelling Results using SOM for PPFW Data Set (Multiple Chlorine Dosing)

Chlorine Decay Model Name:				SOM			
Data Set Name:				Pilbara Water Sample (PPFW)			
Model Parameters				RA0			4.611
				k			0.015
time (hr)	Measured Chlorine Concentration (mg/L)			Predicted Chlorine Concentration Cl(t) (mg/L)			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	2.60	4.59	7.62	3.18	5.37	8.35	1.49
0.17	2.54	4.57	7.88	3.16	5.34	8.30	1.16
0.33	2.43	4.65	7.38	3.13	5.28	8.22	1.58
0.67	2.41	4.44	7.46	3.06	5.16	8.04	1.28
1.00	2.27	4.25	7.36	2.99	5.05	7.87	1.43
2.00	2.10	4.13	6.86	2.81	4.75	7.43	1.22
4.00	1.87	3.82	6.40	2.49	4.26	6.74	0.69
6.00	1.75	3.53	6.00	2.22	3.86	6.22	0.38
8.00	1.65	3.49	5.84	2.00	3.54	5.82	0.13
10.00	1.54	3.41	5.80	1.81	3.28	5.51	0.18
24.00	1.20	2.92	5.28	1.02	2.22	4.41	1.28
48.00	0.74	2.53	4.71	0.48	1.53	3.93	1.67
72.00	0.45	2.24	4.31	0.25	1.24	3.83	1.26
96.00	0.25	1.98	3.89	0.14	1.09	3.80	0.81
120.00	0.16	1.60	3.53	0.08	1.00	3.79	0.44
144.00	0.05	1.35	3.16	0.05	0.94	3.79	0.57
168.00	0.00	1.15	2.97	0.03	0.90	3.79	0.74
192.00	0.00	0.97	2.85	0.02	0.87	3.79	0.89
240.00	0.00	0.59	2.39	0.01	0.83	3.79	2.02
Sum Squared Error (SSE)							19.20
R Squared (R^2)							0.9365

Table.8.9 : Comparison of Chlorine Decay Modelling Results using MSOM for PPFW Data Set (Multiple Chlorine Dosing)

Chlorine Decay Model Name:				MSOM			
Data Set Name:				Pilbara Water Sample (PPFW)			
Model Parameters				FRA0			1.363
				k_FRA			1.845
				SRA0			5.498
				k_SRA			0.004
				Z			0.406
time (hr)	Measured Chlorine Concentration (mg/L)			Predicted Chlorine Concentration Cl(t) (mg/L)			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	2.60	4.59	7.62	2.98	5.05	7.89	0.42
0.17	2.54	4.57	7.88	2.80	4.79	7.57	0.22
0.33	2.43	4.65	7.38	2.59	4.51	7.27	0.06
0.67	2.41	4.44	7.46	2.35	4.23	7.04	0.23
1.00	2.27	4.25	7.36	2.22	4.10	6.96	0.19
2.00	2.10	4.13	6.86	2.02	3.94	6.84	0.04
4.00	1.87	3.82	6.40	1.85	3.79	6.66	0.07
6.00	1.75	3.53	6.00	1.74	3.68	6.49	0.27
8.00	1.65	3.49	5.84	1.66	3.58	6.34	0.25
10.00	1.54	3.41	5.80	1.59	3.48	6.19	0.16
24.00	1.20	2.92	5.28	1.21	2.91	5.38	0.01
48.00	0.74	2.53	4.71	0.81	2.29	4.52	0.10
72.00	0.45	2.24	4.31	0.55	1.90	3.99	0.23
96.00	0.25	1.98	3.89	0.39	1.63	3.64	0.20
120.00	0.16	1.60	3.53	0.27	1.44	3.39	0.06
144.00	0.05	1.35	3.16	0.19	1.31	3.19	0.02
168.00	0.00	1.15	2.97	0.14	1.21	3.04	0.03
192.00	0.00	0.97	2.85	0.10	1.13	2.92	0.04
240.00	0.00	0.59	2.39	0.05	1.02	2.75	0.31
	Sum Squared Error (SSE)						2.91
	R Squared (R^2)						0.9808

Table.8.10 : Comparison of Chlorine Decay Modelling Results using PSOM for PPFW Data Set (Multiple Chlorine Dosing)

Chlorine Decay Model Name:	PSOM	
Data Set Name:	Pilbara Water Sample (PPFW)	
Model Parameters	FRA0	1.441
	SRA0	4.499
	k_FRA	0.461
	k_SRA	0.003

time (hr)	Measured Chlorine Concentration (mg/L)			Predicted Chlorine Concentration Cl(t) (mg/L)						Squared Error
				Cl_FRA(t)	Cl(t)	Cl_FRA(t)	Cl(t)	Cl_FRA(t)	Cl(t)	
0.00	3.20	5.40	8.40	3.20	3.20	5.40	5.40	8.40	8.40	0.00
0.08	2.60	4.59	7.62	3.04	3.04	5.15	5.14	8.02	8.02	0.65
0.17	2.54	4.57	7.88	2.89	2.89	4.92	4.91	7.73	7.71	0.27
0.33	2.43	4.65	7.38	2.68	2.67	4.64	4.62	7.40	7.37	0.06
0.67	2.41	4.44	7.46	2.38	2.36	4.30	4.26	7.10	7.04	0.21
1.00	2.27	4.25	7.36	2.20	2.17	4.14	4.08	7.01	6.91	0.24
2.00	2.10	4.13	6.86	1.93	1.88	3.99	3.88	6.96	6.78	0.12
4.00	1.87	3.82	6.40	1.79	1.70	3.96	3.76	6.96	6.61	0.08
6.00	1.75	3.53	6.00	1.77	1.63	3.96	3.66	6.96	6.45	0.23
8.00	1.65	3.49	5.84	1.76	1.58	3.96	3.57	6.96	6.30	0.22
10.00	1.54	3.41	5.80	1.76	1.54	3.96	3.48	6.96	6.15	0.13
24.00	1.20	2.92	5.28	1.76	1.29	3.96	2.97	6.96	5.36	0.02
48.00	0.74	2.53	4.71	1.76	0.98	3.96	2.36	6.96	4.50	0.13
72.00	0.45	2.24	4.31	1.76	0.75	3.96	1.94	6.96	3.96	0.30
96.00	0.25	1.98	3.89	1.76	0.59	3.96	1.64	6.96	3.60	0.31
120.00	0.16	1.60	3.53	1.76	0.47	3.96	1.42	6.96	3.35	0.16
144.00	0.05	1.35	3.16	1.76	0.37	3.96	1.24	6.96	3.16	0.12
168.00	0.00	1.15	2.97	1.76	0.30	3.96	1.09	6.96	3.02	0.09
192.00	0.00	0.97	2.85	1.76	0.24	3.96	0.98	6.96	2.91	0.06
240.00	0.00	0.59	2.39	1.76	0.16	3.96	0.79	6.96	2.76	0.20
Sum Squared Error (SSE)										3.60
R Squared (R2)										0.9748

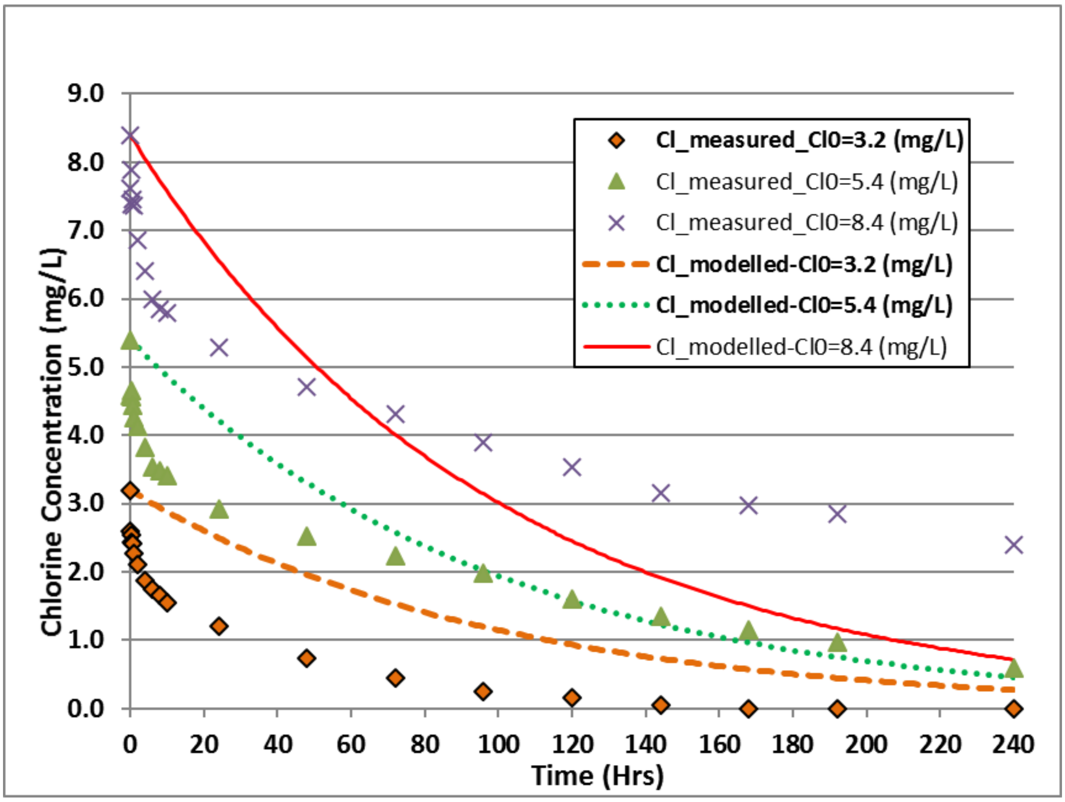


Fig.8.1.: Goodness of data fitting of chlorine decay modelling using FOM for water sample PPFW (Multiple Chlorine Dosing)

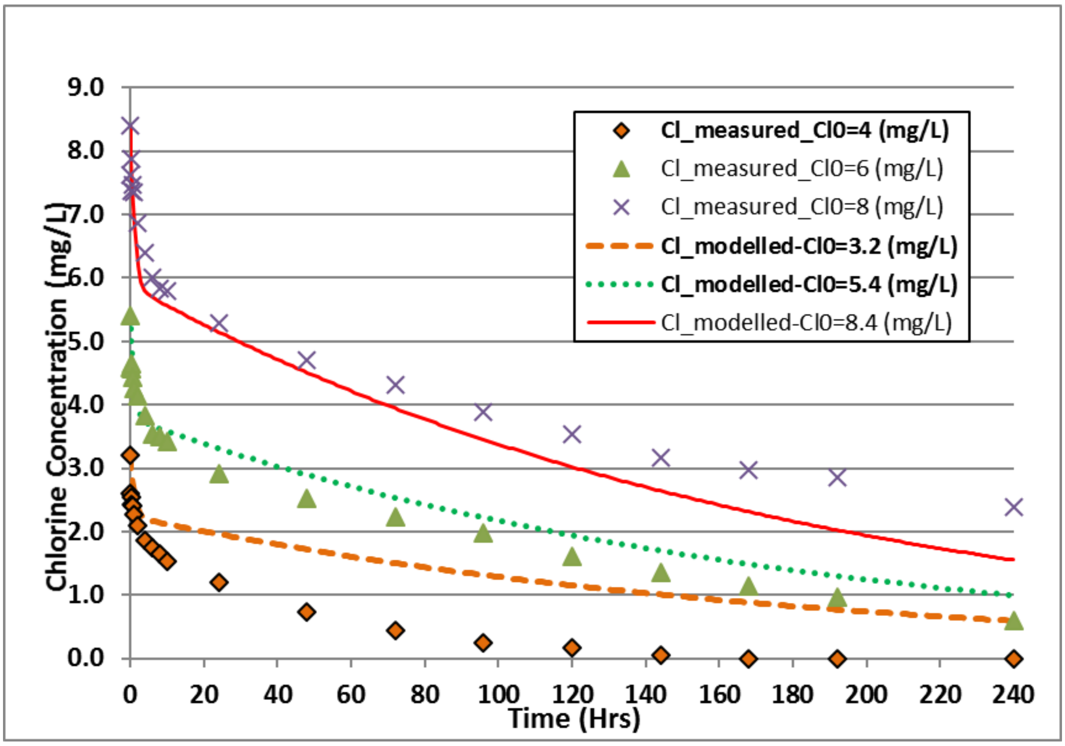


Fig.8.2.: Goodness of data fitting of chlorine decay modelling using PFOM for water sample PPFW (Multiple Chlorine Dosing)

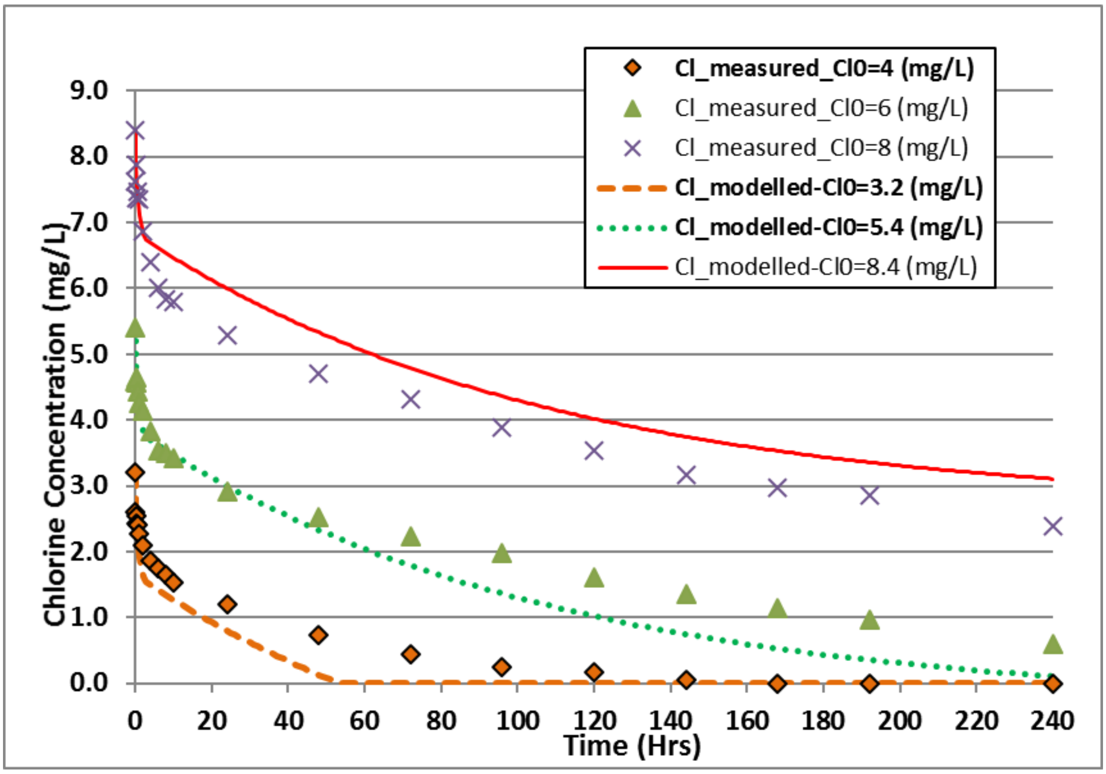


Fig.8.3.: Goodness of data fitting of chlorine decay modelling using MPFOM for water sample PPFW (Multiple Chlorine Dosing)

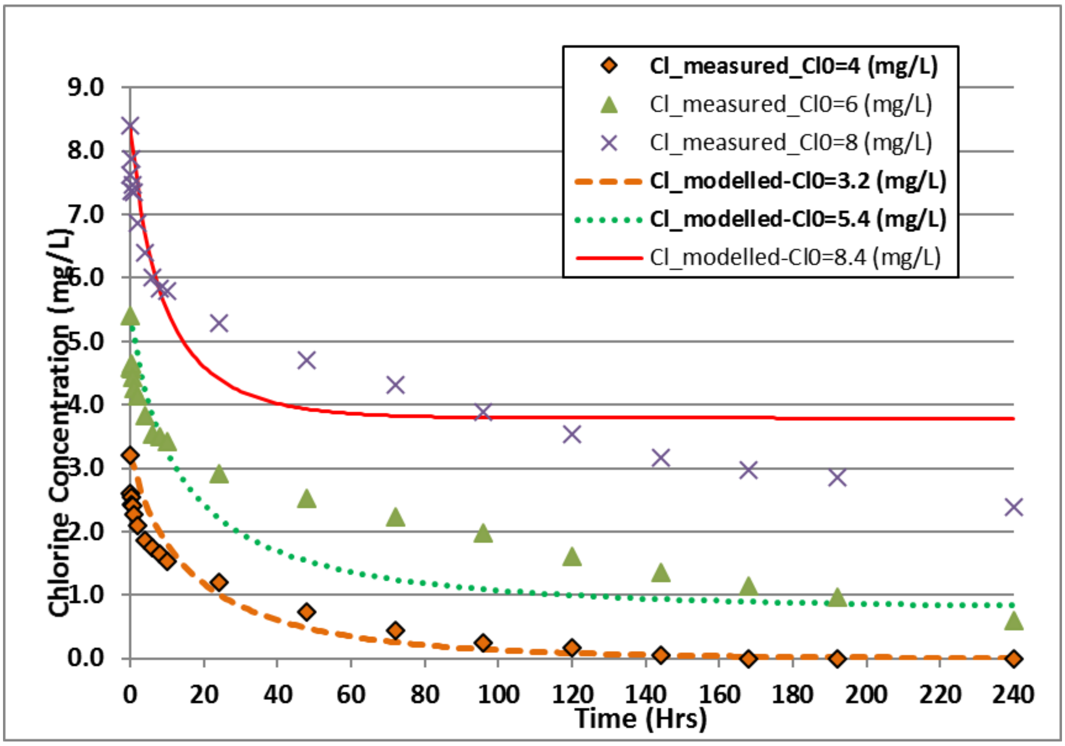


Fig.8.4.: Goodness of data fitting of chlorine decay modelling using SOM for water sample PPFW (Multiple Chlorine Dosing)

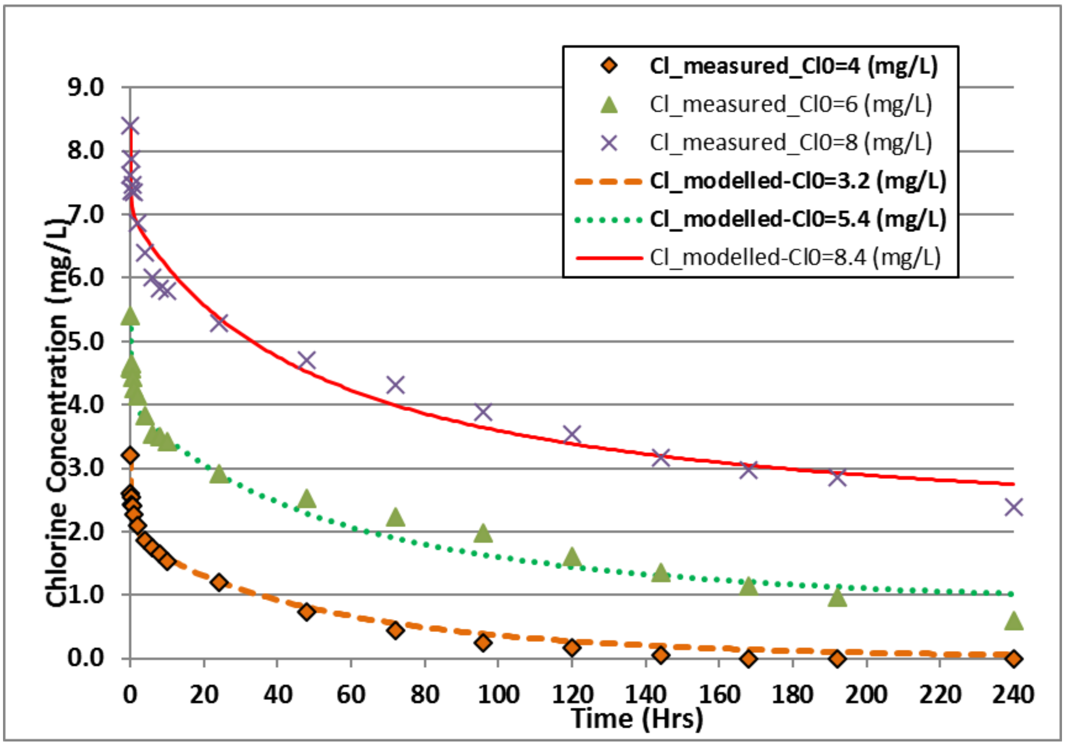


Fig.8.5.: Goodness of data fitting of chlorine decay modelling using MSOM for water sample PPFW (Multiple Chlorine Dosing)

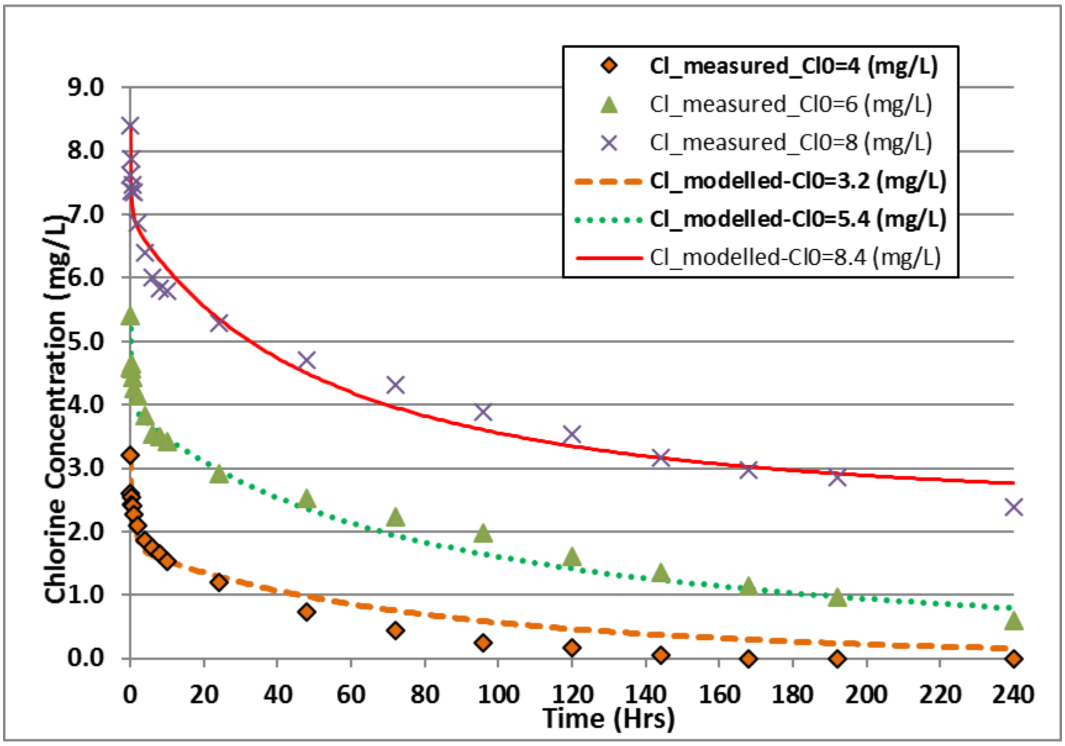


Fig.8.6.: Goodness of data fitting of chlorine decay modelling using PSOM for water sample PPFW (Multiple Chlorine Dosing)

Table.8.11 : Comparison of Chlorine Decay Modelling Results using FOM for Water Sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

Chlorine Decay Model Name:					FOM				
Data Set Name:					Warton et al. (2006)				
Model Parameters					K				0.008
time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)				Squared Error
0.0	4.00	6.00	8.00	10.00	4.00	6.00	8.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	4.00	6.00	7.99	9.99	8.39
0.3	2.39	4.05	5.86	7.79	3.99	5.99	7.98	9.98	15.62
0.5	2.00	3.90	5.78	7.69	3.98	5.98	7.97	9.96	18.17
1	1.85	3.87	5.69	7.59	3.97	5.95	7.93	9.92	19.26
2	1.78	3.79	5.58	7.59	3.95	5.93	7.90	9.88	19.88
2	1.70	3.76	5.58	7.54	3.93	5.90	7.87	9.83	20.07
3	1.70	3.60	5.58	7.44	3.92	5.88	7.83	9.79	20.72
3	1.67	3.60	5.54	7.44	3.90	5.85	7.80	9.75	20.52
4	1.60	3.58	5.50	7.40	3.88	5.83	7.77	9.71	20.77
4	1.58	3.54	5.41	7.28	3.87	5.80	7.74	9.67	21.50
21	1.04	3.09	5.06	6.75	3.36	5.04	6.72	8.39	14.60
30	1.00	3.02	4.98	6.55	3.11	4.67	6.23	7.79	10.29
50	0.84	2.84	4.66	6.04	2.64	3.95	5.27	6.59	5.15
72	0.53	2.38	4.17	5.54	2.19	3.29	4.39	5.49	3.65
96	0.42	2.30	4.17	5.49	1.80	2.69	3.59	4.49	3.38
101	0.33	2.27	4.01	5.34	1.72	2.58	3.45	4.31	3.42
120	0.26	2.12	4.01	5.29	1.47	2.21	2.94	3.68	5.22
144	0.14	1.99	3.89	5.14	1.20	1.81	2.41	3.01	7.90
168	0.11	1.87	3.77	4.88	0.99	1.48	1.97	2.46	9.99
Sum Squared Error (SSE)									248.51
R Squared (R^2)									0.7314

Table.8.12 : Comparison of Chlorine Decay Modelling Results using PFOM for Water Sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

Chlorine Decay Model Name:	PFOM	
Data Set Name:	Warton et al. (2006)	
Model Parameters	k_FRA	10.714
	k_SRA	0.004
	F	0.315

time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)				Squared Error
0.0	4.00	6.00	8.00	10.00	4.00	6.00	8.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	3.27	4.91	6.55	8.19	0.08
0.3	2.39	4.05	5.86	7.79	2.83	4.24	5.65	7.06	0.80
0.5	2.00	3.90	5.78	7.69	2.74	4.11	5.49	6.86	1.38
1	1.85	3.87	5.69	7.59	2.73	4.10	5.46	6.83	1.46
2	1.78	3.79	5.58	7.59	2.73	4.09	5.45	6.82	1.60
2	1.70	3.76	5.58	7.54	2.72	4.08	5.44	6.81	1.71
3	1.70	3.60	5.58	7.44	2.72	4.08	5.44	6.79	1.70
3	1.67	3.60	5.54	7.44	2.71	4.07	5.43	6.78	1.75
4	1.60	3.58	5.50	7.40	2.71	4.06	5.42	6.77	1.86
4	1.58	3.54	5.41	7.28	2.70	4.06	5.41	6.76	1.80
21	1.04	3.09	5.06	6.75	2.55	3.82	5.09	6.37	2.95
30	1.00	3.02	4.98	6.55	2.47	3.70	4.93	6.17	2.76
50	0.84	2.84	4.66	6.04	2.30	3.45	4.60	5.75	2.59
72	0.53	2.38	4.17	5.54	2.13	3.19	4.26	5.32	3.27
96	0.42	2.30	4.17	5.49	1.96	2.93	3.91	4.89	3.19
101	0.33	2.27	4.01	5.34	1.92	2.88	3.84	4.80	3.22
120	0.26	2.12	4.01	5.29	1.80	2.70	3.59	4.49	3.50
144	0.14	1.99	3.89	5.14	1.65	2.48	3.30	4.13	3.89
168	0.11	1.87	3.77	4.88	1.52	2.28	3.04	3.80	3.86
Sum Squared Error (SSE)									43.38
R Squared (R^2)									0.9637

Table.8.13 : Comparison of Chlorine Decay Modelling Results using MPFOM for Water Sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

Chlorine Decay Model Name:					MPFOM				
Data Set Name:					Warton et al. (2006)				
Model Parameters					FRA0				2.292
					SRA0				2.341
					k_FRA				10.000
					k_SRA				0.015
time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)				Squared Error
0.0	4.00	6.00	8.00	10.00	4.00	6.00	8.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	2.74	4.74	6.74	8.74	0.78
0.3	2.39	4.05	5.86	7.79	1.89	3.89	5.89	7.89	0.29
0.5	2.00	3.90	5.78	7.69	1.71	3.71	5.71	7.71	0.13
1	1.85	3.87	5.69	7.59	1.67	3.67	5.67	7.67	0.08
2	1.78	3.79	5.58	7.59	1.66	3.66	5.66	7.66	0.04
2	1.70	3.76	5.58	7.54	1.64	3.64	5.64	7.64	0.03
3	1.70	3.60	5.58	7.44	1.62	3.62	5.62	7.62	0.04
3	1.67	3.60	5.54	7.44	1.61	3.61	5.61	7.61	0.04
4	1.60	3.58	5.50	7.40	1.59	3.59	5.59	7.59	0.05
4	1.58	3.54	5.41	7.28	1.58	3.58	5.58	7.58	0.12
21	1.04	3.09	5.06	6.75	1.09	3.09	5.09	7.09	0.12
30	1.00	3.02	4.98	6.55	0.88	2.88	4.88	6.88	0.15
50	0.84	2.84	4.66	6.04	0.49	2.49	4.49	6.49	0.47
72	0.53	2.38	4.17	5.54	0.18	2.18	4.18	6.18	0.57
96	0.42	2.30	4.17	5.49	0.00	1.94	3.94	5.94	0.56
101	0.33	2.27	4.01	5.34	0.00	1.90	3.90	5.90	0.57
120	0.26	2.12	4.01	5.29	0.00	1.77	3.77	5.77	0.48
144	0.14	1.99	3.89	5.14	0.00	1.65	3.65	5.65	0.45
168	0.11	1.87	3.77	4.88	0.00	1.57	3.57	5.57	0.62
Sum Squared Error (SSE)									5.59
R Squared (R^2)									0.9844

Table.8.14 : Comparison of Chlorine Decay Modelling Results using SOM for Water Sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

Chlorine Decay Model Name:					SOM				
Data Set Name:					Warton et al. (2006)				
Model Parameters					RA0				3.515
					K				0.188
time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)				Squared Error
0.0	4.00	6.00	8.00	10.00	4.00	6.00	8.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	3.80	5.70	7.61	9.52	4.81
0.3	2.39	4.05	5.86	7.79	3.44	5.19	6.96	8.75	4.54
0.5	2.00	3.90	5.78	7.69	3.02	4.63	6.30	8.01	1.96
1	1.85	3.87	5.69	7.59	2.45	3.93	5.53	7.24	0.52
2	1.78	3.79	5.58	7.59	2.07	3.50	5.12	6.87	0.90
2	1.70	3.76	5.58	7.54	1.81	3.23	4.88	6.69	1.51
3	1.70	3.60	5.58	7.44	1.61	3.04	4.74	6.59	1.75
3	1.67	3.60	5.54	7.44	1.46	2.90	4.65	6.54	2.13
4	1.60	3.58	5.50	7.40	1.34	2.80	4.59	6.52	2.28
4	1.58	3.54	5.41	7.28	1.24	2.73	4.55	6.50	2.11
21	1.04	3.09	5.06	6.75	0.56	2.49	4.49	6.49	1.00
30	1.00	3.02	4.98	6.55	0.51	2.49	4.49	6.49	0.77
50	0.84	2.84	4.66	6.04	0.49	2.49	4.49	6.49	0.48
72	0.53	2.38	4.17	5.54	0.49	2.49	4.49	6.49	1.01
96	0.42	2.30	4.17	5.49	0.49	2.49	4.49	6.49	1.13
101	0.33	2.27	4.01	5.34	0.49	2.49	4.49	6.49	1.61
120	0.26	2.12	4.01	5.29	0.49	2.49	4.49	6.49	1.84
144	0.14	1.99	3.89	5.14	0.49	2.49	4.49	6.49	2.53
168	0.11	1.87	3.77	4.88	0.49	2.49	4.49	6.49	3.61
Sum Squared Error (SSE)									36.45
R Squared (R^2)									0.6937

Table.8.15 : Comparison of Chlorine Decay Modelling Results using MSOM for Water Sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

Chlorine Decay Model Name:	MSOM	
Data Set Name:	Warton et al. (2006)	
Model Parameters	FRA0	2.344
	k_FRA	3.489
	SRA0	3.140
	k_SRA	0.004
	Z	0.596

time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)				Squared Error
0.0	4.00	6.00	8.00	10.00	4.00	6.00	8.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	3.06	4.72	6.46	8.26	0.07
0.3	2.39	4.05	5.86	7.79	2.40	4.00	5.80	7.70	0.01
0.5	2.00	3.90	5.78	7.69	2.09	3.74	5.65	7.63	0.05
1	1.85	3.87	5.69	7.59	1.87	3.63	5.61	7.60	0.06
2	1.78	3.79	5.58	7.59	1.78	3.61	5.59	7.58	0.03
2	1.70	3.76	5.58	7.54	1.73	3.59	5.57	7.55	0.03
3	1.70	3.60	5.58	7.44	1.69	3.58	5.55	7.53	0.01
3	1.67	3.60	5.54	7.44	1.67	3.56	5.53	7.50	0.01
4	1.60	3.58	5.50	7.40	1.64	3.55	5.51	7.48	0.01
4	1.58	3.54	5.41	7.28	1.62	3.53	5.49	7.45	0.04
21	1.04	3.09	5.06	6.75	1.29	3.12	4.96	6.81	0.08
30	1.00	3.02	4.98	6.55	1.16	2.94	4.74	6.55	0.09
50	0.84	2.84	4.66	6.04	0.95	2.65	4.38	6.14	0.14
72	0.53	2.38	4.17	5.54	0.77	2.41	4.09	5.82	0.14
96	0.42	2.30	4.17	5.49	0.63	2.21	3.86	5.57	0.15
101	0.33	2.27	4.01	5.34	0.60	2.18	3.82	5.53	0.15
120	0.26	2.12	4.01	5.29	0.52	2.07	3.69	5.39	0.18
144	0.14	1.99	3.89	5.14	0.43	1.95	3.56	5.25	0.21
168	0.11	1.87	3.77	4.88	0.36	1.86	3.45	5.15	0.24
Sum Squared Error (SSE)									1.70
R Squared (R^2)									0.9944

Table.8.16 : Comparison of Chlorine Decay Modelling Results using PSOM for Water Sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

Chlorine Decay Model Name:	PSOM	
Data Set Name:	Warton et al. (2006)	
Model Parameters	FRA0	2.318
	SRA0	2.390
	k_FRA	1.779
	k_SRA	0.004

time (hr)	Measured Chlorine Concentration (mg/L)				Predicted Chlorine Concentration Cl(t) (mg/L)								Squared Error
					Cl_FRA(t)	Cl(t)	Cl_FRA(t)	Cl(t)	Cl_FRA(t)	Cl(t)	Cl_FRA(t)	Cl(t)	
0.0	4.00	6.00	8.00	10.00	4.00	4.00	6.00	6.00	8.00	8.00	10.00	10.00	0.00
0.1	3.25	4.68	6.42	8.09	3.09	3.09	4.77	4.77	6.52	6.52	8.33	8.32	0.10
0.3	2.39	4.05	5.86	7.79	2.32	2.31	3.98	3.97	5.82	5.80	7.74	7.72	0.02
0.5	2.00	3.90	5.78	7.69	1.93	1.92	3.74	3.72	5.69	5.67	7.68	7.65	0.05
1	1.85	3.87	5.69	7.59	1.73	1.72	3.68	3.65	5.68	5.63	7.68	7.62	0.07
2	1.78	3.79	5.58	7.59	1.69	1.67	3.68	3.63	5.68	5.61	7.68	7.58	0.04
2	1.70	3.76	5.58	7.54	1.68	1.66	3.68	3.62	5.68	5.59	7.68	7.55	0.02
3	1.70	3.60	5.58	7.44	1.68	1.65	3.68	3.60	5.68	5.56	7.68	7.52	0.01
3	1.67	3.60	5.54	7.44	1.68	1.64	3.68	3.59	5.68	5.54	7.68	7.49	0.00
4	1.60	3.58	5.50	7.40	1.68	1.63	3.68	3.57	5.68	5.52	7.68	7.46	0.01
4	1.58	3.54	5.41	7.28	1.68	1.62	3.68	3.56	5.68	5.49	7.68	7.43	0.03
21	1.04	3.09	5.06	6.75	1.68	1.41	3.68	3.13	5.68	4.89	7.68	6.67	0.18
30	1.00	3.02	4.98	6.55	1.68	1.32	3.68	2.96	5.68	4.66	7.68	6.41	0.23
50	0.84	2.84	4.66	6.04	1.68	1.15	3.68	2.65	5.68	4.28	7.68	6.00	0.28
72	0.53	2.38	4.17	5.54	1.68	0.99	3.68	2.40	5.68	4.00	7.68	5.73	0.28
96	0.42	2.30	4.17	5.49	1.68	0.86	3.68	2.20	5.68	3.79	7.68	5.56	0.35
101	0.33	2.27	4.01	5.34	1.68	0.84	3.68	2.16	5.68	3.76	7.68	5.54	0.37
120	0.26	2.12	4.01	5.29	1.68	0.75	3.68	2.04	5.68	3.65	7.68	5.46	0.40
144	0.14	1.99	3.89	5.14	1.68	0.67	3.68	1.92	5.68	3.56	7.68	5.40	0.46
168	0.11	1.87	3.77	4.88	1.68	0.59	3.68	1.83	5.68	3.49	7.68	5.36	0.54
Sum Squared Error (SSE)													3.44
R Squared (R2)													0.9859

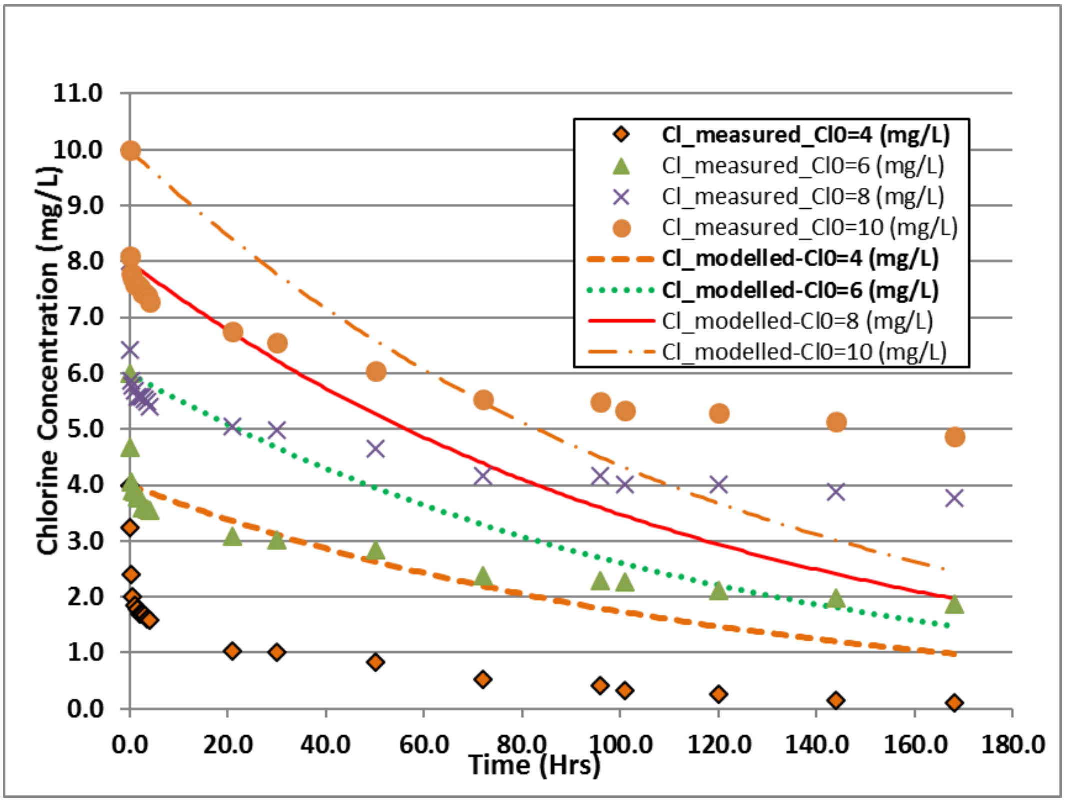


Fig.8.7.: Goodness of data fitting of chlorine decay modelling using FOM for water sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

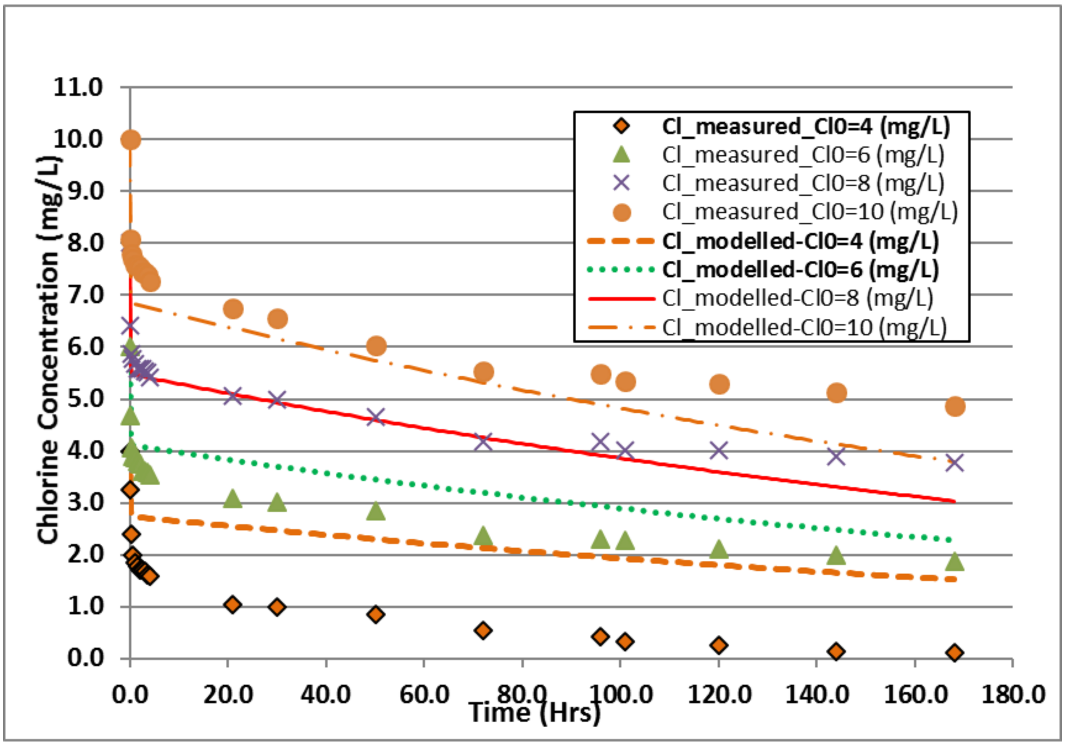


Fig.8.8.: Goodness of data fitting of chlorine decay modelling using PFOM for water sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

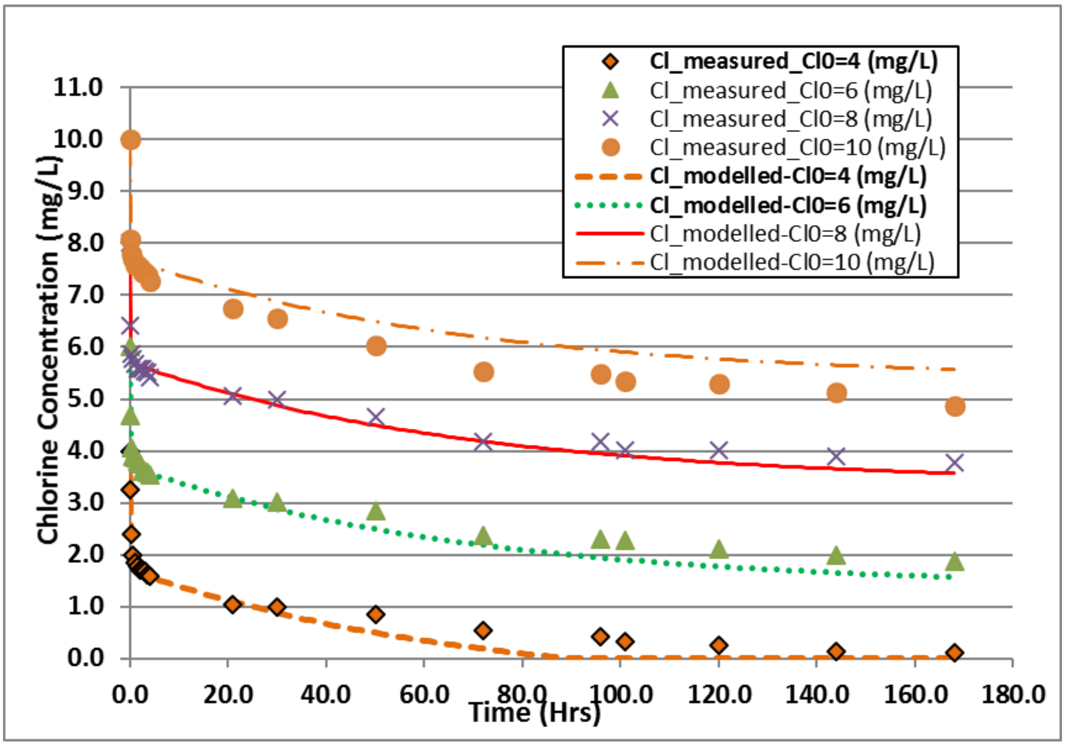


Fig.8.9.: Goodness of data fitting of chlorine decay modelling using MPFOM for water sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

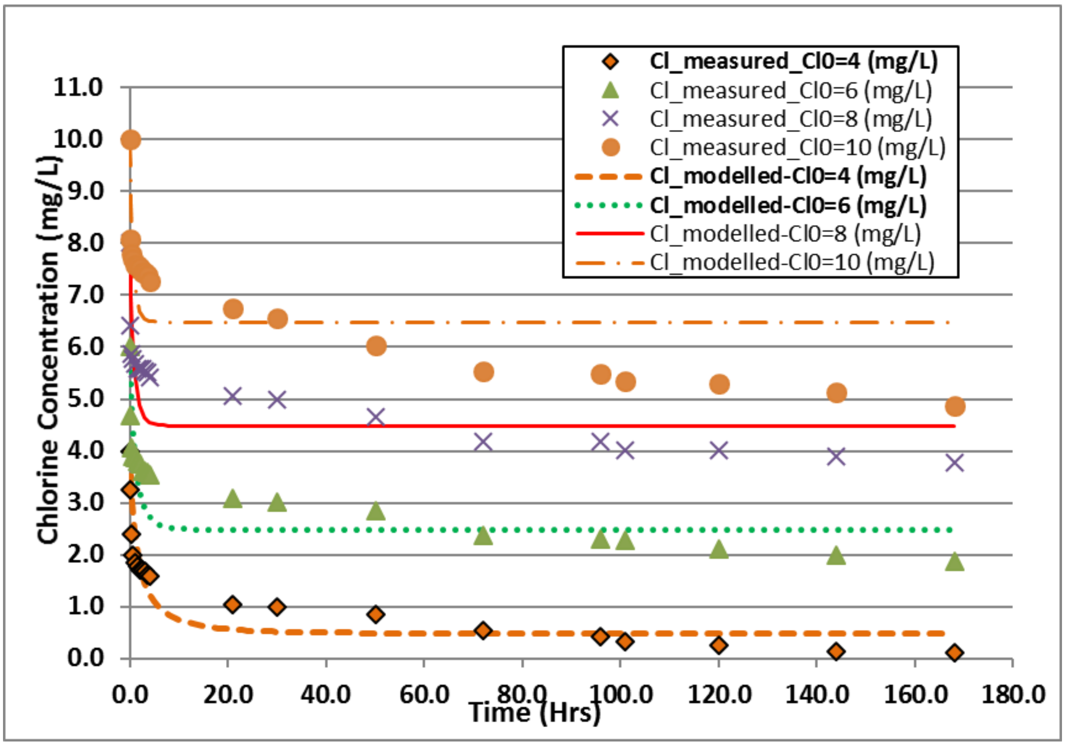


Fig.8.10.: Goodness of data fitting of chlorine decay modelling using SOM for water sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

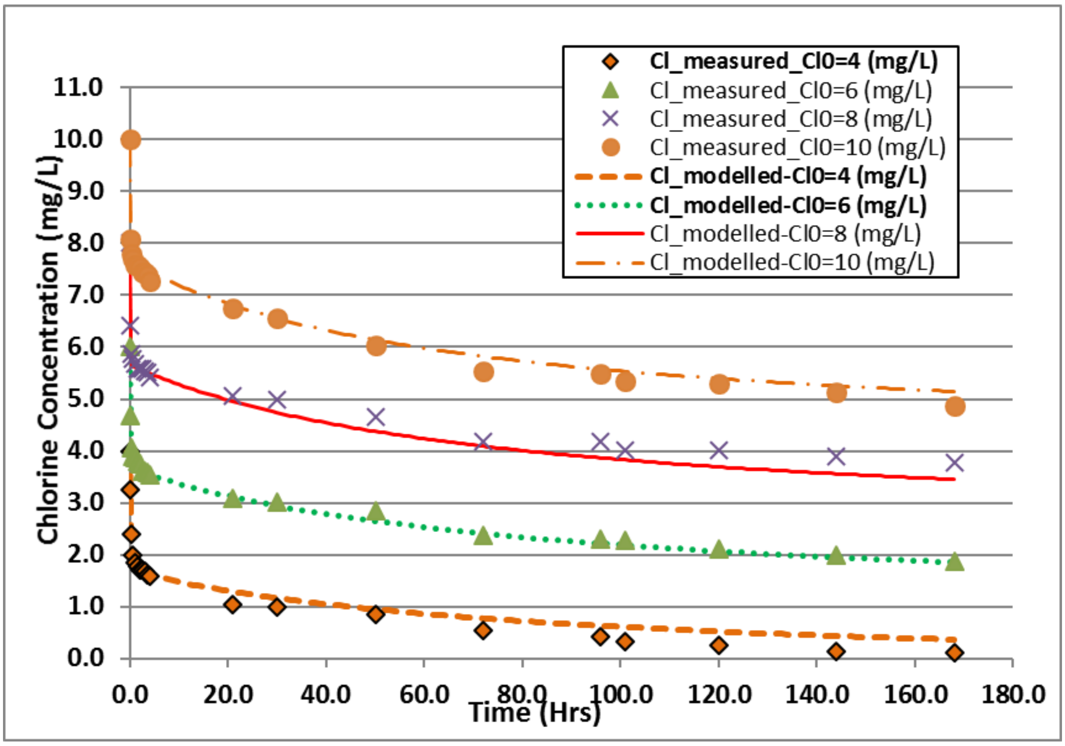


Fig.8.11. : Goodness of data fitting of chlorine decay modelling using MSOM for water sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

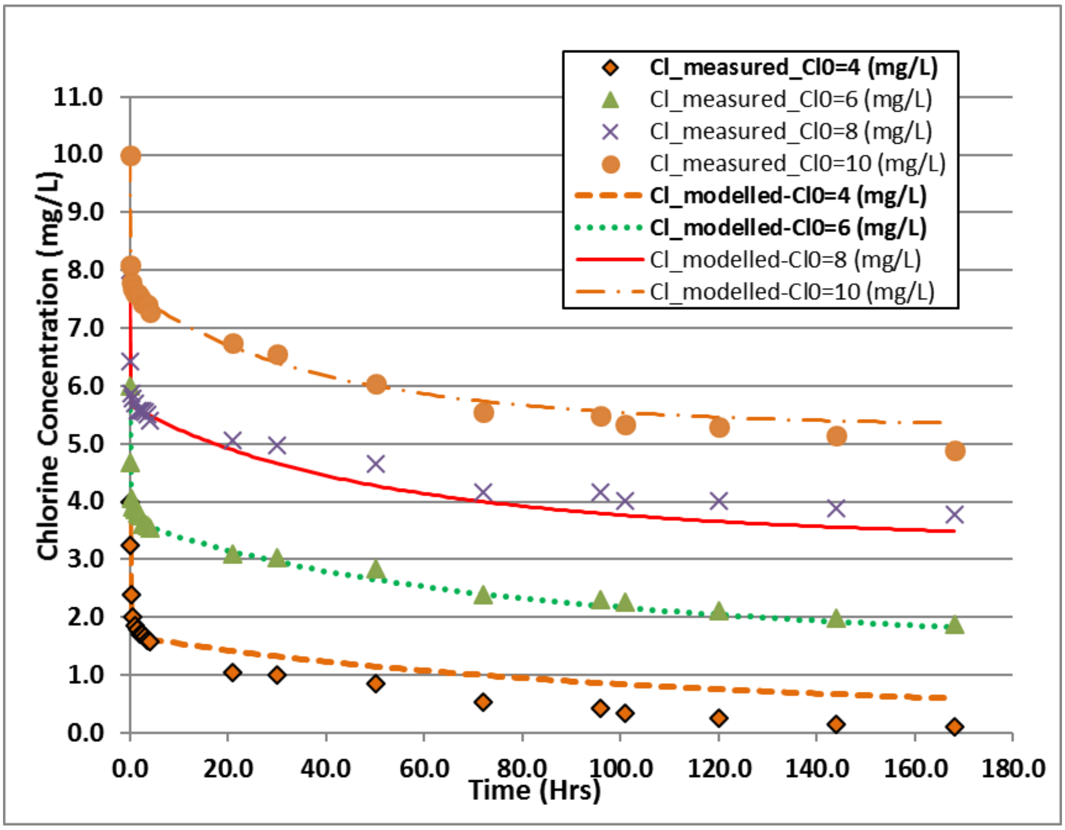


Fig.8.12. : Goodness of data fitting of chlorine decay modelling using PSOM for water sample from Warton et al. (2006)'s Study (Multiple Chlorine Dosing)

Table.8.17 : Comparison of SSE and R^2 Values for all Nominated Models for Water Samples PPFW and Warton et al. (2006) (Multiple Chlorine Dosing)

Chlorine Decay Model Name	Data Set Name				Ranking
	PPFW		Warton et al. (2006)		
	Sum Squared Error (SSE)	R Squared (R^2)	Sum Squared Error (SSE)	R Squared (R^2)	
FOM	65.14	0.9116	248.51	0.7314	6
PFOM	16.02	0.9754	43.38	0.9637	4
MPFOM	9.99	0.9715	5.59	0.9844	3
SOM	19.20	0.9365	36.45	0.6937	5
MSOM	2.91	0.9808	1.70	0.9944	1
PSOM	3.60	0.9748	3.44	0.9859	2

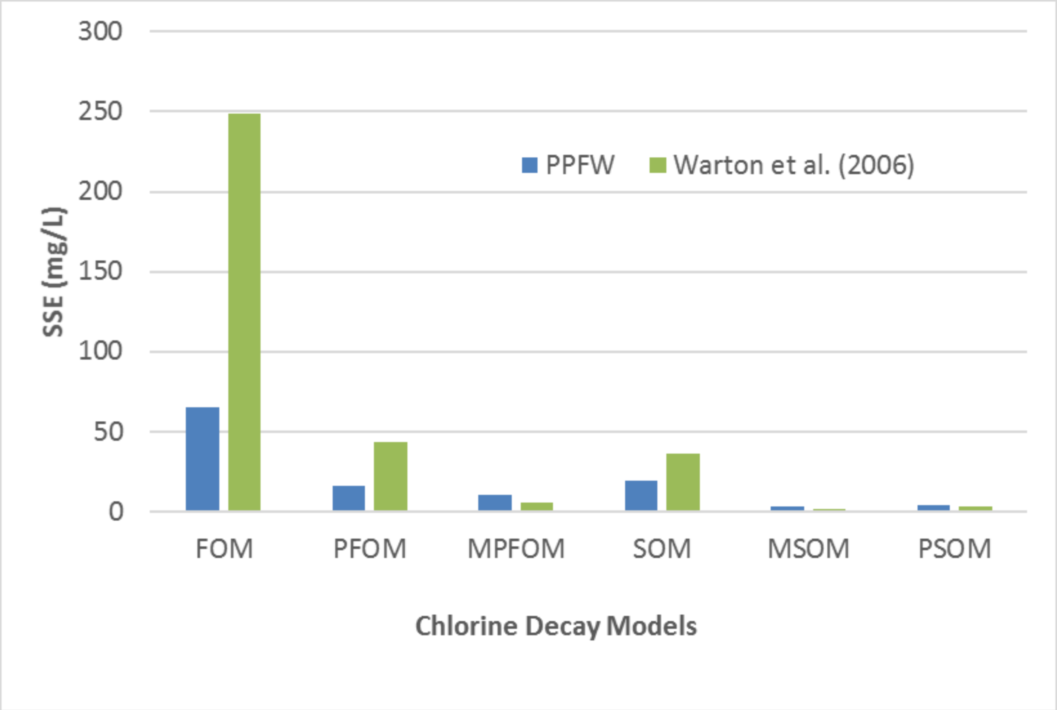


Fig.8.13. : Comparison of SSE Values for all Nominated Models for Water Samples PPFW and Warton et al. (2006) (Multiple Chlorine Dosing)

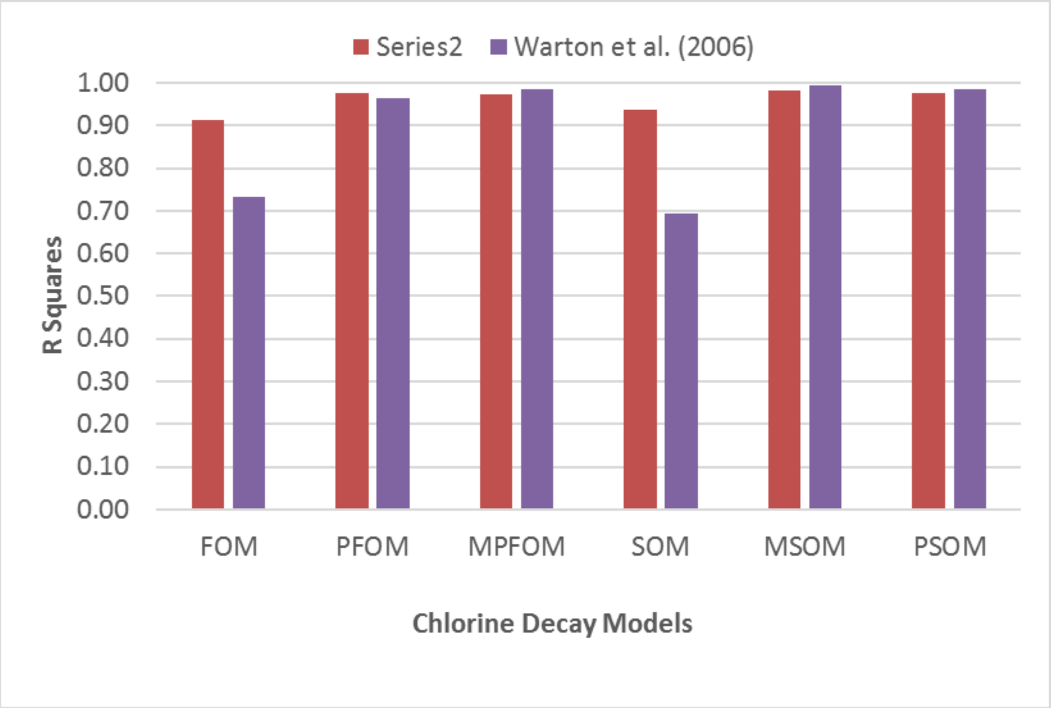


Fig.8.14.: Comparison of R Squared (R^2) Values for all Nominated Models for Water Samples PPFW and Warton et al. (2006) (Multiple Chlorine Dosing)

8.4. Conclusion

In this chapter, six previously discussed process-based chlorine decay models were evaluated for the accuracy of their results for multiple dosing scenario. The nominated models are:

- First Order Model (FOM)
- Parallel First Order Model (PFOM)
- Modified Parallel First Order Model (MPFOM)
- Second Order Model (SOM)
- Modified Second Order Model (MSOM)
- Parallel Second Order Model (PSOM)

In order to compare the accuracy of the abovementioned process-based chlorine decay models, two sets of data were used. One data set was obtained from the chlorine decay test of a water sample taken from post filtration section at Pilbara Water Treatment Plant (labelled as PPFW). Another set of chlorine decay data was extracted from the research work performed by Warton et al. (2006). Data analysis for chlorine decay modelling of the selected data was performed using prepopulated Excel spreadsheets. Solver Add-in was used to undertake parameter estimation for the nominated modelling approaches. The sum of squared errors (SSE) between actual and predicted data was calculated for each data set for all models. The SSEs, which are calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy. The models were ranked based on the results of their SSE values. Lower the SSE of the model was, the higher the model was ranked. MSOM and PSOM were ranked first and second amongst all nominated models. Although MSOM was ranked better than PSOM with regards to accuracy of the predicted chlorine residuals, it should be noted that MSOM contained five parameters compared to only four parameters of the PSOM and thus MSOM produced more accurate results than PSOM due to having more model parameters. Also, it was noticed that the difference in accuracy of the results between MSOM and PSOM was negligible. Therefore, it was concluded that the PSOM was the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water for multiple dosing scenarios.

9. Evaluation of Process-Based Chlorine Decay Models against Temperature Variation for Multiple Dosing Scenario

9.1. Introduction

Temperature variation is one of the important factors that influence the rate of chlorine decay. Annual temperature variation of more than 20°C for water in distribution systems is common. Therefore, chlorine dosing needs to be adjusted substantially between seasons to maintain residuals within desired limits. As a result, the impact from seasonal temperature variation of water should be managed with chlorine decay models. In fact, the chlorine decay models should be able to predict chlorine residuals accurately during various seasons of the year and with different water temperature.

The adjustment of initial chlorine dosing due to seasonal temperature variation does not normally occur within a short period of time and, thus, the impact cannot be dealt with using the multiple dosing scenario. However, Arrhenius equation can be used to estimate the effects of temperature variation on chlorine decay. This can be done by including temperature dependence parameter, i.e. activation energy (E) / universal gas constant (R), in formulation of the chlorine decay models. It is an important criterion for chlorine decay models to be able to accurately model temperature variation effects on chlorine decay.

Evaluation of some chlorine decay models against temperature variation has been studied before for single chlorine dosing scenarios. However, performance of process-based chlorine decay models for multiple dosing scenarios at various temperatures has not yet been assessed. In this chapter, the previously discussed process-based chlorine decay models will be evaluated for the accuracy of their results for multiple dosing scenarios at different temperatures. In order to compare the accuracy of different models the weighted error (sum of errors or chi^2- chi squared) between experimental and model data (χ^2) can be used as a measure of accuracy of a chlorine decay model. The weighted error (sum of errors or chi^2- chi squared) can be defined as follows:

$$\chi^2(\mathrm{p}) = \sum_{i=1}^{n} \left(\frac{f_{meas\_i} - f_i(p)}{\sigma_{meas\_i}}\right)^2 \qquad (1)$$

where f_{meas_i} is the ith measured value, $f_i(p)$ is the calculated value from the model using parameter values p and σ_{meas_i} is the estimated standard deviation of f_{meas_i}.

9.2. Material and Methods:

Two different sets of chlorine decay data will be used for the accuracy assessment of the six nominated process-based chlorine decay models. The two sets of data were acquired by undertaking chlorine decay tests on water sample taken from Harding Dam Water Treatment Plant at temperatures of 25°C and 35°C. Table 9.1 shows water quality characteristics of the sample obtained from Pilbara treatment plant.

Table.9.1 : Water Quality Characteristics for the PPFW Sample

Sample label	**Description**	**water quality characteristics**		
		DOC (mg/L)	**UV254**	**pH**
PPFW	Pilbara Post-Filtration Water	2.16	0.022	7.65

Water samples were stored in the prepared chlorine-demand-free amber bottles. N,N-diethyl-p-phenylenediamine (DPD) colorimetric method was used to conduct chlorine measurements using Lovibond® pocket colorimeter. Repeated tests were undertaken for each experiment to minimise the effects of variations in the water quality and also to reduce the impact from potential human errors. The test results were compared for consistency. For chlorination of the samples, diluted standard sodium hypochlorite solution was used. In order to confirm the initial chlorine concentration (initial dose), several experiments with de-ionized water were conducted before undertaking the main tests. Prepared chlorine-demand-free plastic bottles were used to store the water samples. Temperature condition of the samples was maintained constant by keeping the samples inside the water bath. Before starting any sampling for the experiments, all containers and glassware were cleaned with de-ionized water to ensure that no chlorine demand was present. Duplicate analysis was performed on each sample to get an accuracy of ±0.05 mg/L, and the average was reported.

The chlorine decay tests for PPFW sample were conducted for three initial chlorine concentrations (3.2 mg/L, 5.4 mg/L and 8.4 mg/L) at both 25˚C and 35˚C. Tables 9.2 and 9.3 show the free chlorine decay test data for the PPFW sample at 25˚C and 35˚C, respectively.

Table.9.2 : Free Chlorine Decay Test Data for PPFW Sample (**25˚C**)

Time (hrs)	Initial Chlorine Concentration (Dose) (mgL^{-1})		
	3.2	**5.4**	**8.4**
	Chlorine Residual (mgL^{-1})		
0	3.20	5.40	8.40
0.08	2.60	4.59	7.62
0.17	2.54	4.57	7.88
0.33	2.43	4.65	7.38
0.67	2.41	4.44	7.46
1	2.27	4.25	7.36
2	2.10	4.13	6.86
4	1.87	3.82	6.40
6	1.75	3.53	6.00
8	1.65	3.49	5.84
10	1.54	3.41	5.80
24	1.20	2.92	5.28
48	0.74	2.53	4.71
72	0.45	2.24	4.31
96	0.25	1.98	3.89
120	0.16	1.60	3.53
144	0.05	1.35	3.16
168	0.00	1.15	2.97
192	0.00	0.97	2.85
240	0.00	0.59	2.39

Table.9.3 : Free Chlorine Decay Test Data for PPFW Sample (**35˚C**)

Time (hrs)	Initial Chlorine Concentration (Dose) (mgL^{-1})		
	3.2	**5.4**	**8.4**
	Chlorine Residual (mgL^{-1})		
3.20	5.40	8.40	3.20
2.62	4.42	7.44	2.62
2.41	4.12	7.24	2.41
2.27	4.04	7.16	2.27
2.20	3.80	6.80	2.20
2.13	3.80	6.64	2.13
1.75	3.72	6.24	1.75
1.52	3.30	5.96	1.52
1.32	3.00	5.52	1.32
1.28	2.86	5.36	1.28
1.15	2.62	5.20	1.15
0.61	1.93	4.38	0.61
0.15	0.81	2.68	0.15
0.00	0.42	1.40	0.00
0.00	0.16	0.66	0.00
0.00	0.00	0.37	0.00
0.00	0.00	0.13	0.00
0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00

9.2.1. Data Analysis

Data analysis for chlorine decay modelling of the selected data has been performed using prepopulated Excel spreadsheets. Solver Add-in is used to undertake parameter estimation for the nominated modelling approaches. For each model, parameters were defined based on the analytical solution/formula of the model. An initial value was assigned for each model parameter. An extra parameter of E/R was also defined for each model to account for temperature effect. Reaction rates for the nominated temperatures were then calculated based on Arrhenius equation.

Data analysis could not be completed for MPFOM and MSOM due to occurrence of calculation error while parameter estimation was being undertaken by Solver Add-in. It was identified that the reason for errors was due to high number of model parameters and also limitation of Excel Spreadsheets for performing calculations of big numbers. As a result, evaluation of temperature variation was not completed for these two models and was only undertaken for FOM, SOM, PFOM and PSOM. For all these models, the chlorine residuals have been predicted for each data set over the entire retention time with maximum one hour intervals. The sum of squared errors (SSE) between actual and predicted data has been calculated for each data set for all models. The SSEs, which are calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy. R squared values are also calculated and compared for each set of data for all nominated models.

9.3. Results and Discussions

Tables 9.4 to 9.7 show the results of chlorine decay modelling with temperature variation and multiple chlorine dosing scenarios for the nominated models using the water sample PPFW from Pilbara Post- Filtration Water Treatment Plant at temperatures of 25°C and 35°C. The Sum Squared Errors (SSE) for the results predicted by FOM for this data set with various initial chlorine concentrations of 3.2, 5.4 and 8.4 mg/L is calculated to be 105.08 which appears to be the highest SSE value compared to other results. SSE values corresponding to PFOM, SOM and PSOM for the same water sample are calculated to be 24.75, 65.23 and 8.62, respectively. As can be seen from Tables 9.4 to 9.7, the R^2 values calculated for the nominated models (FOM, PFOM, SOM and PSOM) are 0.9308, 0.9753, 0.9489 and 0.9674, respectively.

One of the reasons that PFOM and PSOM generate more accurate results compared to FOM and SOM is that the parallel first and second order models (PFOM and PSOM) contain more parameters that need to be estimated and therefore that have more flexibility to fit the data.

Table 9.8 compares the SSE and R^2 values estimated using nominated chlorine decay models for the selected water sample and the ranking of each model. Also, Figure 9.9 presents the SSE values graphically for all models and the selected water sample. Figure 9.10 shows the R^2 values calculated for all nominated chlorine decay models. As can be seen from Table 9.8 and Figure 9.9 PSOM is ranked first amongst all nominated models. Therefore, it is concluded that the PSOM is the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water with effect of multiple chlorine dosing and temperature variation. Figures 9.1 to 9.8 show the goodness of data fitting of chlorine decay modelling using the nominated models.

Table.9.4 : Results of Chlorine Decay Modelling using FOM for PPFW Data Set at Temperatures of 25°C and 35°C (Multiple Chlorine Dosing)

Chlorine Decay Model Name:				FOM			
Data Set Name:				Pilbara Water Sample (PPFW)			
Model Parameters (To be estimated)				k_25			0.0103
				E/R			15640.85
Model Parameter (Reaction rate to be calculated using Arrhenius equation)				k_35			0.0564
time (hr)	Predicted Chlorine Concentration Cl(t) (mg/L) at 25°C			Predicted Chlorine Concentration Cl(t) (mg/L) at 35°C			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	3.20	5.40	8.39	3.19	5.38	8.36	3.69
0.17	3.19	5.39	8.39	3.17	5.35	8.32	4.62
0.33	3.19	5.38	8.37	3.14	5.30	8.25	5.62
0.67	3.18	5.36	8.34	3.08	5.20	8.09	6.62
1.00	3.17	5.34	8.31	3.02	5.10	7.94	7.10
2.00	3.13	5.29	8.23	2.86	4.82	7.50	8.35
4.00	3.07	5.18	8.06	2.55	4.31	6.70	8.71
6.00	3.01	5.08	7.90	2.28	3.85	5.99	9.45
8.00	2.95	4.97	7.74	2.04	3.44	5.35	8.40
10.00	2.89	4.87	7.58	1.82	3.07	4.78	7.96
24.00	2.50	4.22	6.57	0.83	1.39	2.17	10.26
48.00	1.96	3.30	5.13	0.21	0.36	0.56	6.95
72.00	1.53	2.58	4.01	0.06	0.09	0.14	3.06
96.00	1.19	2.02	3.14	0.01	0.02	0.04	1.88
120.00	0.93	1.58	2.45	0.00	0.01	0.01	1.90
144.00	0.73	1.23	1.92	0.00	0.00	0.00	2.04
168.00	0.57	0.96	1.50	0.00	0.00	0.00	2.53
192.00	0.45	0.75	1.17	0.00	0.00	0.00	3.05
240.00	0.27	0.46	0.72	0.00	0.00	0.00	2.90
Sum Squared Error (SSE)							105.08
R Squared (R^2)							0.9308

Table.9.5 : Results of Chlorine Decay Modelling using PFOM for PPFW Data Set at Temperatures of 25°C and 35°C (Multiple Chlorine Dosing)

Chlorine Decay Model Name:	PFOM	
Data Set Name:	Pilbara Water Sample (PPFW)	
Model Parameters (To be estimated)	k_FRA_25	1.2305
	k_SRA_25	0.0059
	f	0.2736
	E/R	12695.76
Model Parameters (Reaction rates to be calculated using Arrhenius equation)	k_FRA_35	4.9068
	k_SRA_35	0.0236

time (hr)	Predicted Chlorine Concentration Cl(t) (mg/L) at 25°C			Predicted Chlorine Concentration Cl(t) (mg/L) at 35°C			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	3.12	5.26	8.18	2.91	4.91	7.64	1.40
0.17	3.03	5.12	7.96	2.70	4.55	7.08	0.85
0.33	2.90	4.90	7.62	2.48	4.18	6.51	0.83
0.67	2.70	4.55	7.09	2.32	3.92	6.09	0.77
1.00	2.57	4.33	6.74	2.28	3.84	5.98	0.95
2.00	2.37	4.00	6.23	2.22	3.74	5.82	0.89
4.00	2.28	3.84	5.98	2.12	3.57	5.55	0.94
6.00	2.24	3.79	5.89	2.02	3.41	5.30	1.02
8.00	2.22	3.74	5.82	1.92	3.25	5.05	1.05
10.00	2.19	3.70	5.75	1.84	3.10	4.82	1.35
24.00	2.02	3.40	5.29	1.32	2.23	3.47	2.33
48.00	1.75	2.95	4.59	0.75	1.27	1.97	2.29
72.00	1.52	2.56	3.99	0.43	0.72	1.12	1.71
96.00	1.32	2.22	3.46	0.24	0.41	0.63	1.52
120.00	1.14	1.93	3.00	0.14	0.23	0.36	1.44
144.00	0.99	1.67	2.60	0.08	0.13	0.20	1.33
168.00	0.86	1.45	2.26	0.04	0.07	0.12	1.36
192.00	0.75	1.26	1.96	0.03	0.04	0.07	1.43
240.00	0.56	0.95	1.48	0.01	0.01	0.02	1.28
Sum Squared Error (SSE)							24.75
R Squared (R^2)							0.9753

Table.9.6 : Results of Chlorine Decay Modelling using SOM for PPFW Data Set at Temperatures of 25°C and 35°C (Multiple Chlorine Dosing)

Chlorine Decay Model Name:	SOM	
Data Set Name:	Pilbara Water Sample (PPFW)	
Model Parameters (To be estimated)	RA0	7.4942
	k_25	0.0031
	E/R	13895.14
Model Parameter (Reaction rate to be calculated using Arrhenius equation)	k_35	0.0139

time (hr)	Predicted Chlorine Concentration Cl(t) (mg/L) at 25°C			Predicted Chlorine Concentration Cl(t) (mg/L) at 35°C			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	3.19	5.39	8.38	3.17	5.36	8.33	3.56
0.17	3.19	5.38	8.37	3.14	5.31	8.25	4.29
0.33	3.18	5.36	8.34	3.09	5.22	8.12	4.97
0.67	3.15	5.32	8.27	2.99	5.04	7.85	5.27
1.00	3.13	5.28	8.21	2.89	4.88	7.61	5.21
2.00	3.06	5.16	8.03	2.62	4.45	6.97	5.18
4.00	2.92	4.94	7.70	2.18	3.74	5.97	4.69
6.00	2.80	4.74	7.39	1.83	3.21	5.24	4.87
8.00	2.68	4.54	7.11	1.55	2.78	4.68	4.32
10.00	2.57	4.37	6.85	1.32	2.44	4.24	4.05
24.00	1.94	3.39	5.48	0.49	1.17	2.66	4.36
48.00	1.26	2.36	4.14	0.11	0.45	1.77	1.59
72.00	0.85	1.74	3.36	0.03	0.20	1.42	1.36
96.00	0.59	1.34	2.86	0.01	0.10	1.23	1.92
120.00	0.42	1.05	2.51	0.00	0.05	1.13	1.97
144.00	0.30	0.84	2.26	0.00	0.02	1.06	2.00
168.00	0.21	0.68	2.06	0.00	0.01	1.01	2.12
192.00	0.15	0.56	1.90	0.00	0.01	0.98	2.04
240.00	0.08	0.38	1.67	0.00	0.00	0.95	1.46
Sum Squared Error (SSE)							65.23
R Squared (R^2)							0.9489

Table.9.7 : Results of Chlorine Decay Modelling using PSOM for PPFW Data Set at Temperatures of 25°C and 35°C (Multiple Chlorine Dosing)

Chlorine Decay Model Name:	PSOM	
Data Set Name:	Pilbara Water Sample (PPFW)	
Model Parameters (To be estimated)	FRA0	1.6922
	SRA0	11.3071
	k_FRA_25	0.2507
	k_SRA_25	0.0006
	E/R	13016.83
Model Parameters (Reaction rates to be calculated using Arrhenius equation)	k_FRA_35	1.0352
	k_SRA_35	0.0027

time (hr)	Predicted Chlorine Concentration Cl(t) (mg/L) at 25°C			Predicted Chlorine Concentration Cl(t) (mg/L) at 35°C			Squared Error
0.00	3.20	5.40	8.40	3.20	5.40	8.40	0.00
0.08	3.09	5.23	8.14	2.82	4.81	7.57	1.13
0.17	2.99	5.06	7.89	2.52	4.41	7.11	0.55
0.33	2.82	4.81	7.57	2.18	4.03	6.78	0.37
0.67	2.55	4.44	7.14	1.81	3.72	6.59	0.32
1.00	2.35	4.20	6.92	1.65	3.62	6.51	0.49
2.00	1.98	3.84	6.66	1.45	3.49	6.32	0.28
4.00	1.66	3.63	6.52	1.34	3.29	5.97	0.13
6.00	1.53	3.55	6.42	1.26	3.11	5.64	0.26
8.00	1.46	3.50	6.33	1.19	2.93	5.35	0.29
10.00	1.42	3.45	6.24	1.12	2.77	5.07	0.25
24.00	1.27	3.12	5.67	0.75	1.91	3.63	0.78
48.00	1.07	2.65	4.86	0.38	1.07	2.25	0.46
72.00	0.90	2.27	4.22	0.20	0.62	1.49	0.31
96.00	0.76	1.95	3.69	0.11	0.37	1.02	0.49
120.00	0.65	1.68	3.26	0.06	0.22	0.72	0.50
144.00	0.55	1.46	2.89	0.03	0.13	0.51	0.50
168.00	0.47	1.27	2.58	0.02	0.08	0.37	0.54
192.00	0.40	1.11	2.31	0.01	0.05	0.27	0.54
240.00	0.29	0.85	1.88	0.00	0.02	0.15	0.44
Sum Squared Error (SSE)							8.62
R Squared (R^2)							0.9674

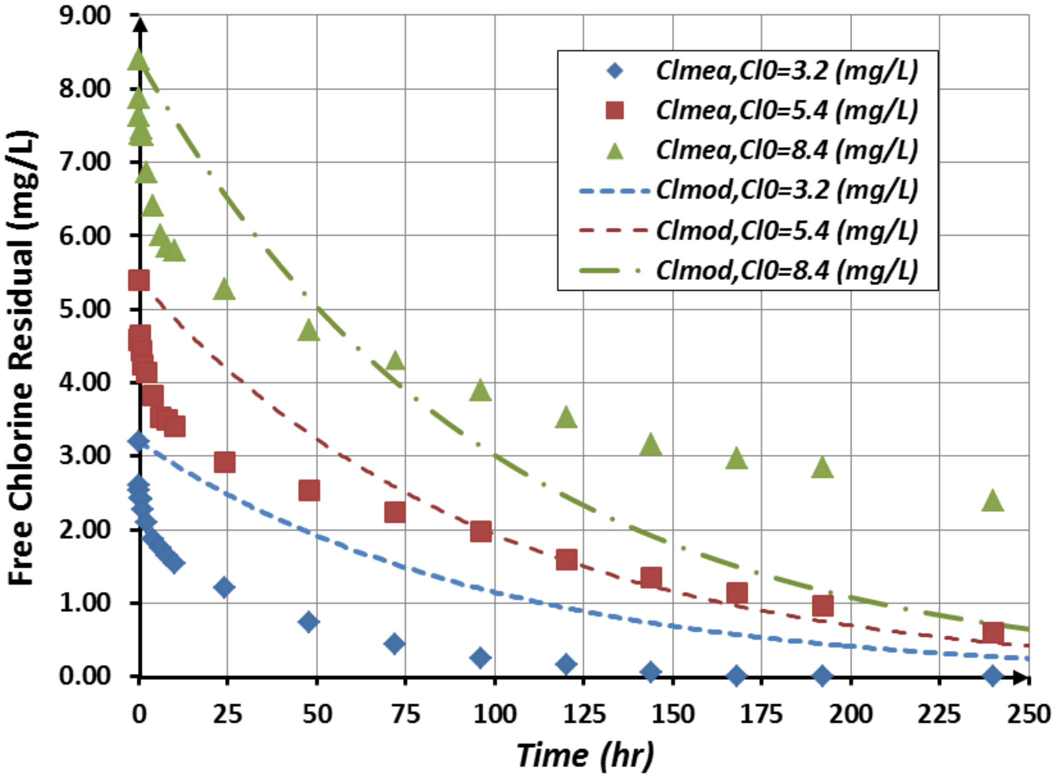


Fig.9.1.: Goodness of data fitting of chlorine decay modelling using FOM for water sample PPFW at 25°C (Effect of Multiple Dosing and Temperature Variation)

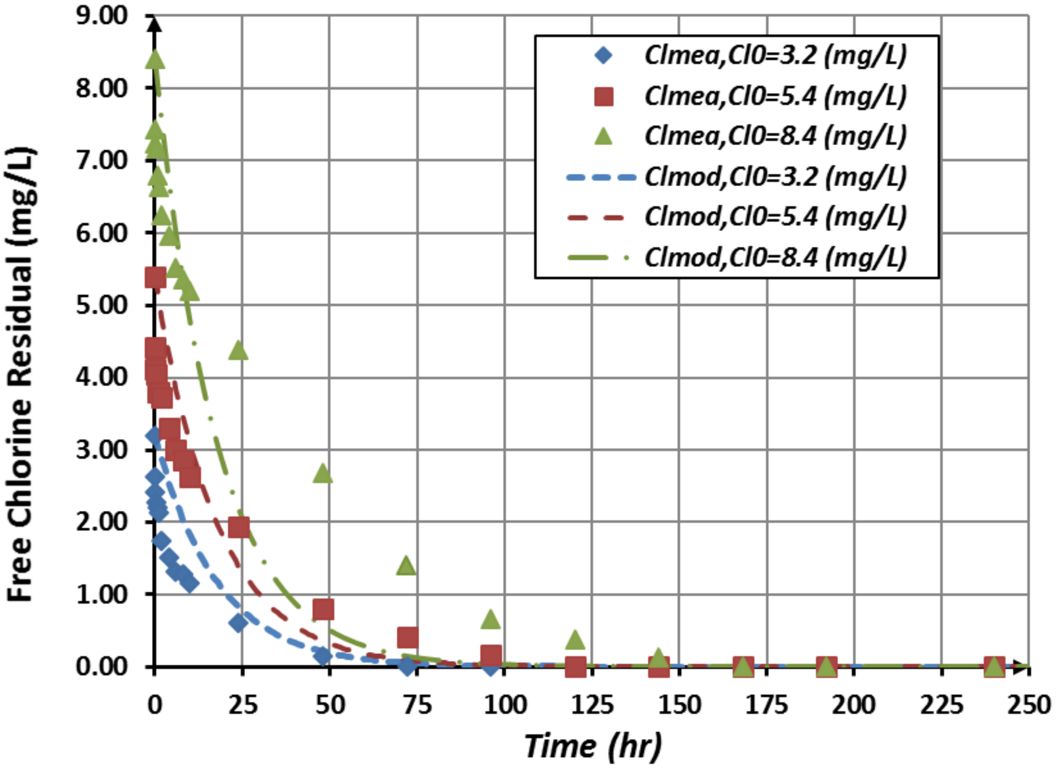


Fig.9.2.: Goodness of data fitting of chlorine decay modelling using FOM for water sample PPFW at 35°C (Effect of Multiple Dosing and Temperature Variation)

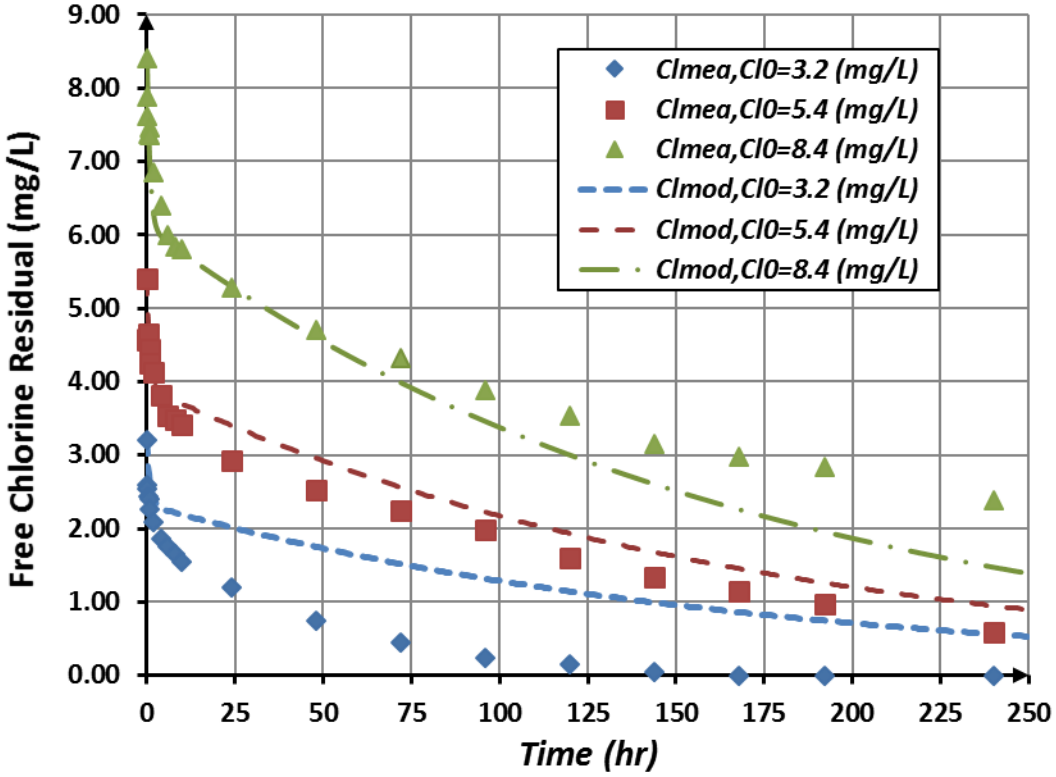


Fig.9.3.: Goodness of data fitting of chlorine decay modelling using PFOM for water sample PPFW at 25°C (Effect of Multiple Dosing and Temperature Variation)

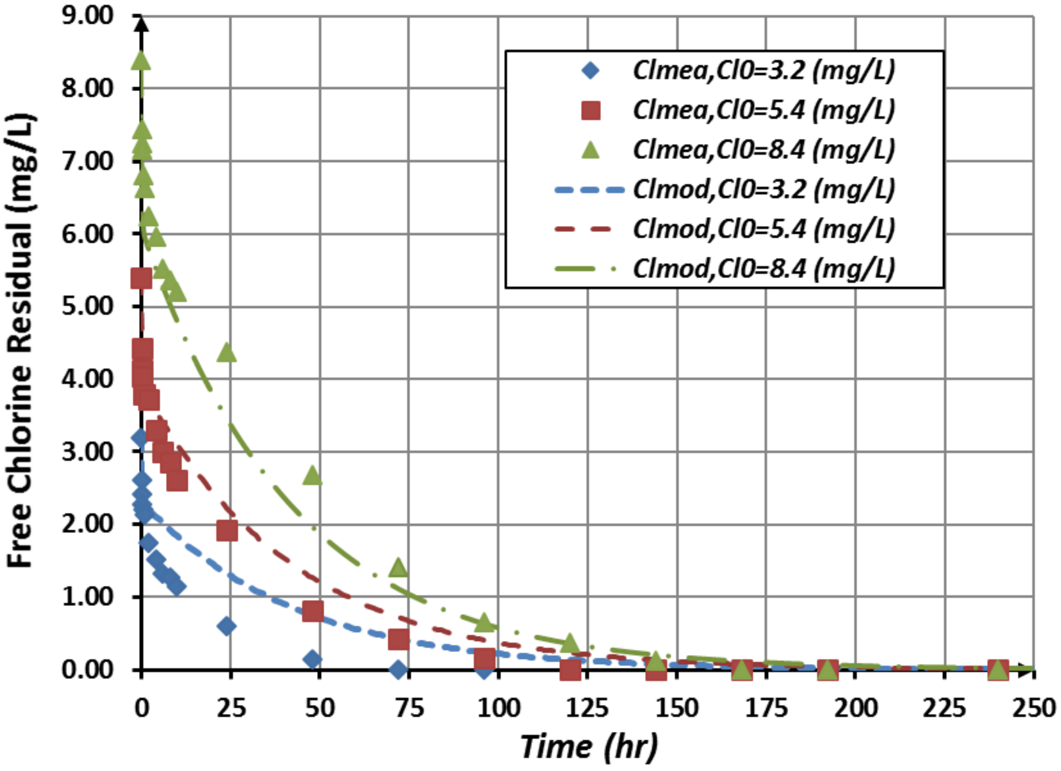


Fig.9.4.: Goodness of data fitting of chlorine decay modelling using PFOM for water sample PPFW at 35°C (Effect of Multiple Dosing and Temperature Variation)

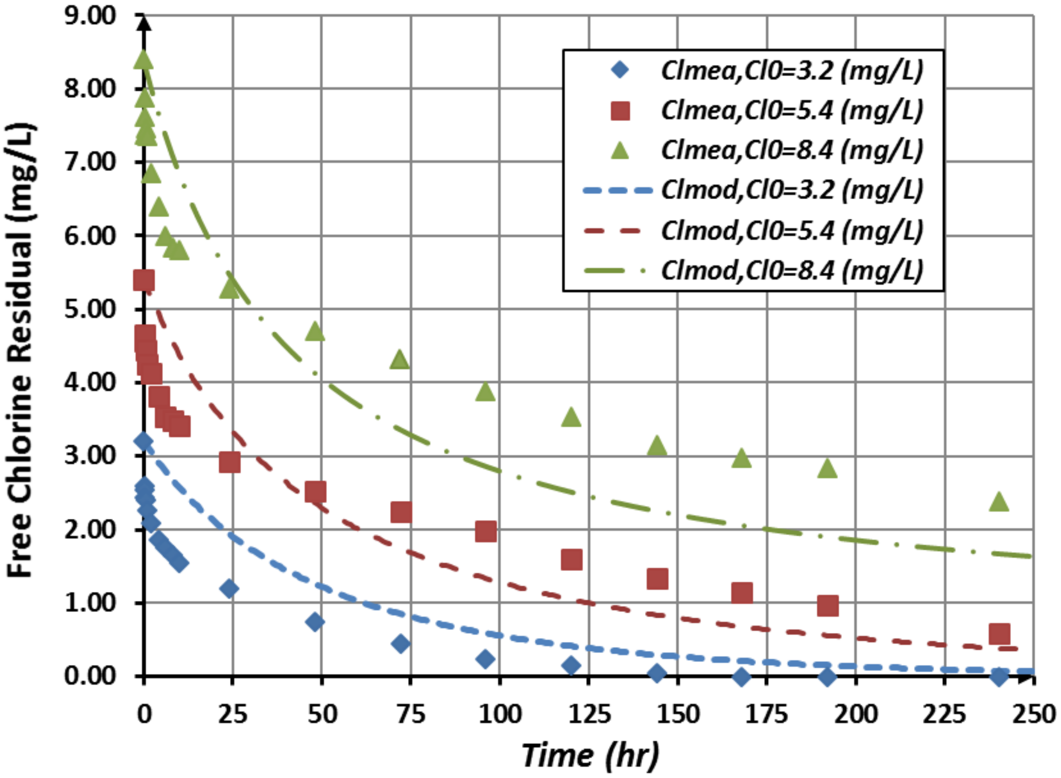


Fig.9.5.: Goodness of data fitting of chlorine decay modelling using SOM for water sample PPFW at 25°C (Effect of Multiple Dosing and Temperature Variation)

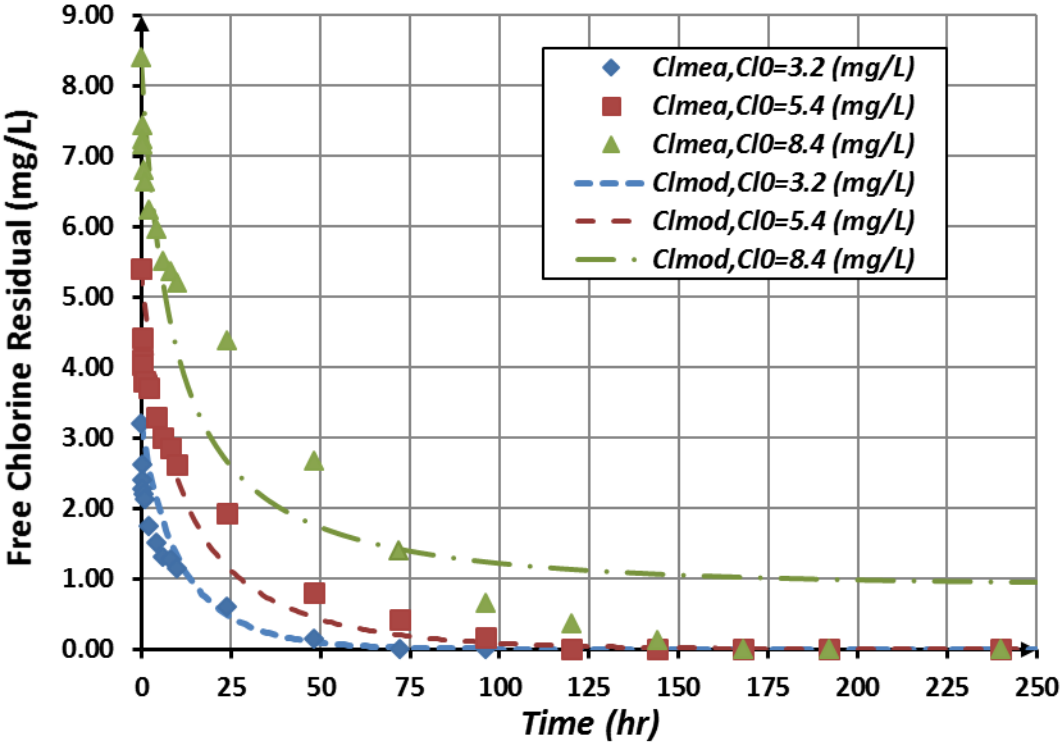


Fig.9.6.: Goodness of data fitting of chlorine decay modelling using SOM for water sample PPFW at 35°C (Effect of Multiple Dosing and Temperature Variation)

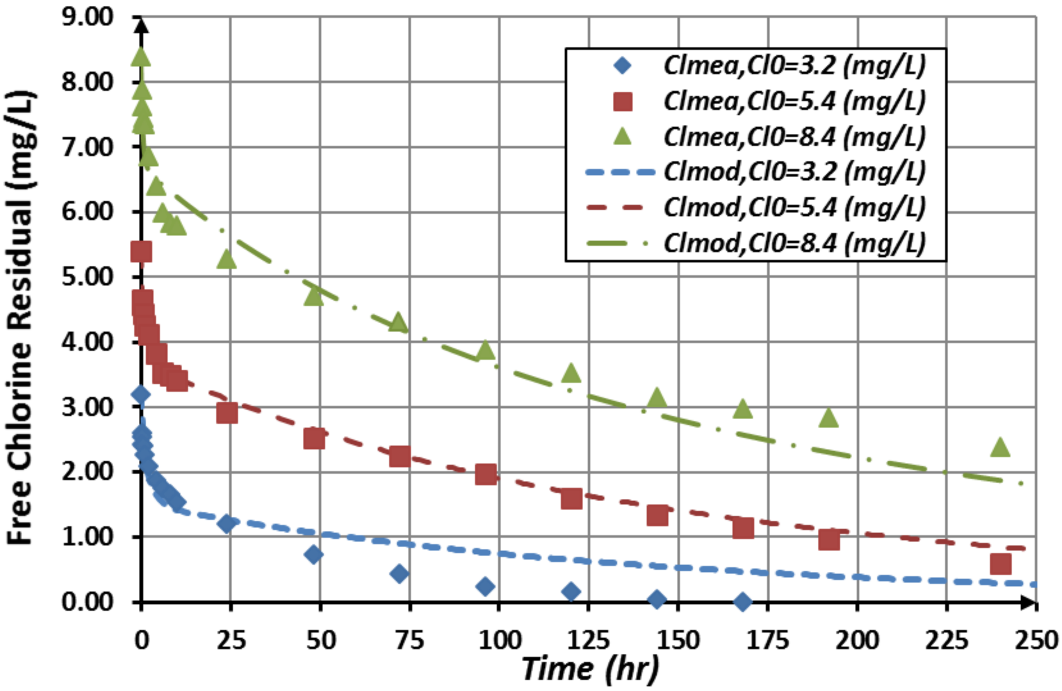


Fig.9.7.: Goodness of data fitting of chlorine decay modelling using PSOM for water sample PPFW at 25°C (Effect of Multiple Dosing and Temperature Variation)

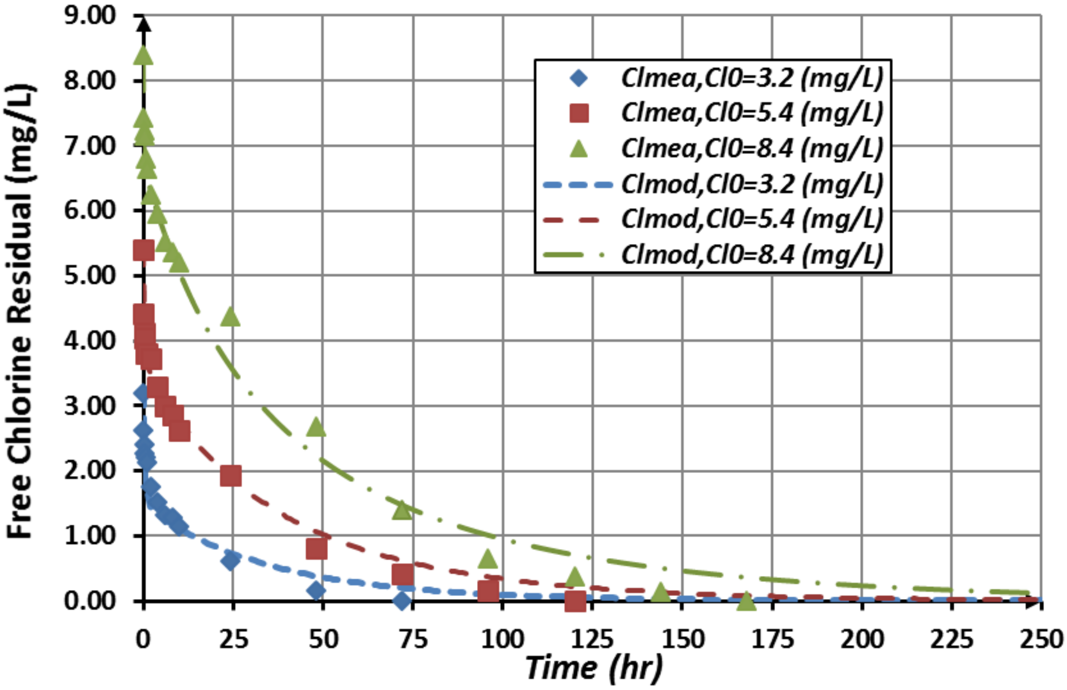


Fig.9.8.: Goodness of data fitting of chlorine decay modelling using PSOM for water sample PPFW at 35°C (Effect of Multiple Dosing and Temperature Variation)

Table.9.8 : Comparison of SSE and R^2 Values for Nominated Models for the Water Sample PPFW (Effect of Multiple Dosing and Temperature Variation)

Chlorine Decay Model Name	Data Set Name		Model Ranking
	PPFW		
	Sum Squared Error (SSE)	R Squared (R^2)	
FOM	105.08	0.9308	4
PFOM	24.75	0.9753	2
SOM	65.23	0.9489	3
PSOM	8.62	0.9674	1

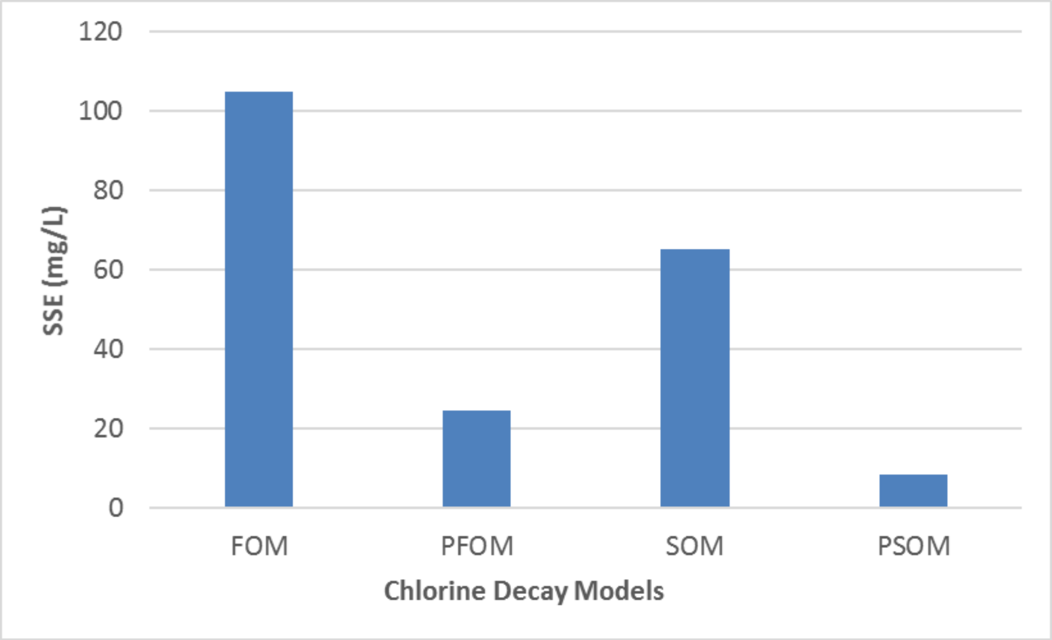


Fig.9.9.: Comparison of SSE Values for Nominated Models for the Water Sample PPFW (Effect of Multiple Dosing and Temperature Variation)

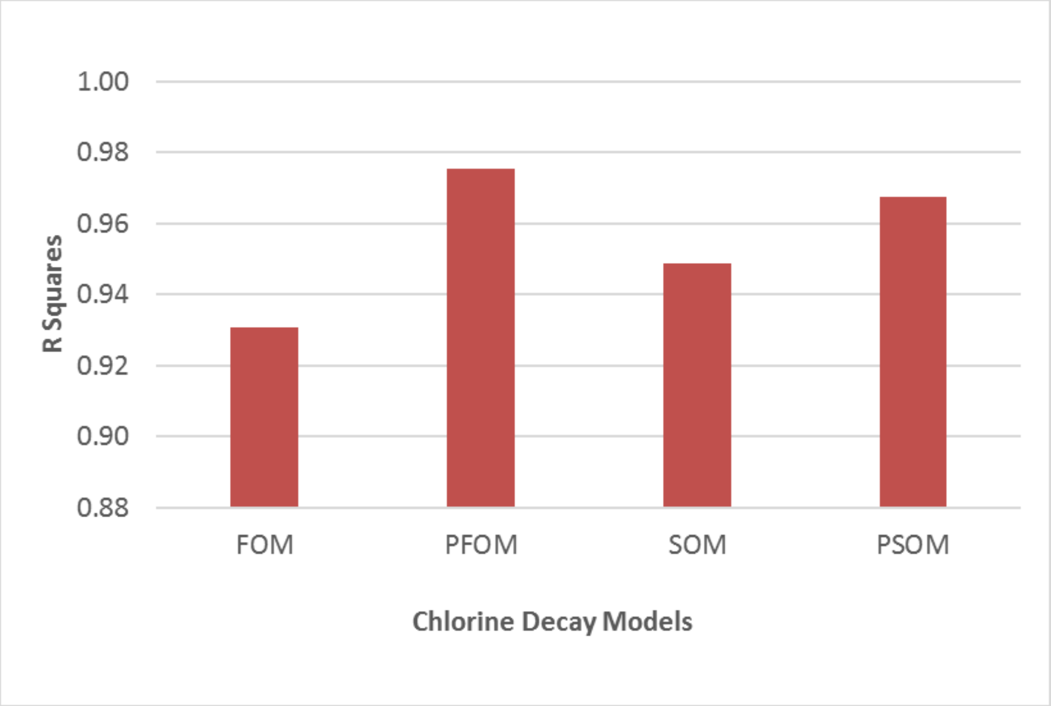


Fig.9.10.: Comparison of R Squared (R^2) Values for Nominated Models for the Water Sample PPFW (Effect of Multiple Dosing and Temperature Variation)

9.4. Conclusion

In this chapter, six previously discussed process-based chlorine decay models were evaluated for the accuracy of their results considering simultaneous effects of multiple chlorine dosing and temperature variation. The nominated models are:

- First Order Model (FOM)
- Parallel First Order Model (PFOM)
- Modified Parallel First Order Model (MPFOM)
- Second Order Model (SOM)
- Modified Second Order Model (MSOM)
- Parallel Second Order Model (PSOM)

In order to compare the accuracy of the abovementioned process-based chlorine decay models, two different sets of chlorine decay data were used for the accuracy assessment of the six nominated process-based chlorine decay models. The two sets of data were acquired by undertaking chlorine decay tests on water sample taken from Harding Dam Water Treatment Plant at temperatures of 25°C and 35°C.

Data analysis for chlorine decay modelling of the selected data has been performed using prepopulated Excel spreadsheets. Solver Add-in is used to undertake parameter estimation for the nominated modelling approaches. For each model, parameters were defined based on the analytical solution/formula of the model. An initial value was assigned for each model parameter. An extra parameter of E/R was also defined for each model to account for temperature effect. Reaction rates for the nominated temperatures were then calculated based on Arrhenius equation.

Data analysis could not be completed for MPFOM and MSOM due to occurrence of calculation error while parameter estimation was being undertaken by Solver Add-in. It was identified that the reason for errors was due to high number of model parameters and also limitation of Excel Spreadsheets for performing calculations of big numbers. As a result, evaluation of temperature variation was not completed for these two models and was only undertaken for FOM, SOM, PFOM and PSOM. For all these models, the chlorine residuals have been predicted for each data set over the entire retention time with maximum one hour intervals. The sum of squared errors (SSE) between actual and predicted data was calculated for each data set for all models. The SSEs, which were calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy. R squared values were also calculated and compared for each set of data for all nominated models.

The models were ranked based on the results of their SSE values. Lower the SSE of the model was, the higher the model was ranked. PSOM were ranked first. Therefore, it is concluded that the PSOM is the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water with effect of multiple chlorine dosing and temperature variation.

10. Modelling chlorine decay and DBPs formation

10.1. Introduction:

As mentioned in previous chapters, Drinking water should be disinfected to remove any potential threat from pathogenic microorganisims that can cause water-borne diseases. Chlorine is widely used as an effective disinfectant in the final step of most water treatment processes due to its low cost and high efficacy.

Chlorine as a non-selective and reasonably strong oxidant reacts with a wide range of organic and inorganic substances including natural organic matters (NOMs) and microorganisms including bacteria, viruses and fungi.

The initial concentration of the chlorine, however, should be high enough to achieve an adequate inactivation of microorganisms before the treated water reaches the first customer (primary disinfection). In addition, a minimum concentration of disinfectant should always be maintained at the periphery of the distribution system to inhibit microbial regrowth (secondary disinfection). According to current water quality guidelines, a minimum concentration of free chlorine higher than 0.2mg/L is required.

Chlorine also reacts with inorganic and organic matters and its reaction with those substances other than microorganisms is known as the main reason for its decay over time. The reaction between chlorine and NOMs results in the production of disinfection by-products (DBPs), some of which has been recognised as potentially carcinogenic or toxic substances and harmful to human health.

The guideline for total trihalomethanes (TTHMs) in the US has been reduced to 0.08mg/L and further reduction is expected. In Australia, water utilities are considering the technical feasibility of reducing TTHM and other chlorinated by-products such as halo-acetic acids (HAAs). As DBPs are the products of chlorine reaction with organic substances, the chlorine concentration should be minimised to reduce the formation of DBPs.

One practical method to control the formation of DBPs, except the enhancement of water treatment processes, is to predict their formation along the distribution system accurately. As it is proved that there is a linear relationship between DBPs formation and the chlorine demand, it could also be done by precisely predicting the chlorine decay in the distribution system. However, chlorine decay behaviour has been proved to be significantly affected by water quality characteristics such as total organic carbon

(TOC), dissolved organic carbon (DOC), pH and temperature. There are also several evidences of how different types of treatment processes and hydraulic and non-hydraulic conditions of the distribution system may influence the chlorine decay profile (Clark and Sivaganesan, 2002). As a result, having a robust process-based chlorine decay model, which can precisely predict the chlorine residual, while considering all influencing factors, is more desirable and broadly emphasized.

In this chapter, using the results of chlorine decay modelling in bulk water (application of the parallel second order model for the laboratory experimental data), the chlorine decay and DBPs formation will be modelled within a pilot water distribution system in Western Australia. The results afterwards will be compared to the on-site measurements.

10.2. Conceptual Background of the Process-Based Model

Introducing EPANET, Rossman (2000) proposed a process-based model for modelling chlorine decay in water distribution systems. Process-based (or mechanistic) models consists of a set of variables (such as residual at key locations, reservoir volumes and demands) which should be related through a set of dynamic process equations based on physical and chemical principles (e.g., conservation of mass for water and chemical constituents, mass-action kinetics in chemical reactions). These equations can be solved to obtain the time-varying concentrations of chlorine and other variables within the system. The process equations, however, contain parameters (coefficients) to be estimated from appropriate experimental data or from on-site measurements.

When chlorinated water, which contains NOM, travels throughout a pipe, two significant physical phases could be considered: a mobile bulk water phase and a fixed pipe surface phase. Bulk phase contains the chemical or biological components that exist within the bulk water and are transported through the system with the average water velocity. Surface phase species are components that are attached into or be sloughed from the pipe wall and are thus considered as immobile. Surface species, such as corrosion products, can enter the water body, but any increment in reaction rate due to them is also included in the wall reaction. Figure 1 illustrates an example of bulk phase chlorine (HOCl) reacting with bulk phase NOM (natural organic matter) to produce a bulk phase disinfectant by-product (DBP), while also oxidizing ferrous iron to ferric iron in the fixed surface phase at the pipe wall (Shang et al., 2008). According to this concept, two independent series of reactions could be considered to occur between chlorine and other substances in the water during the travelling time throughout the distribution system: one is the reaction between chlorine and bulk species in the water and the other is the chlorine interaction with the pipe wall and biofilm.

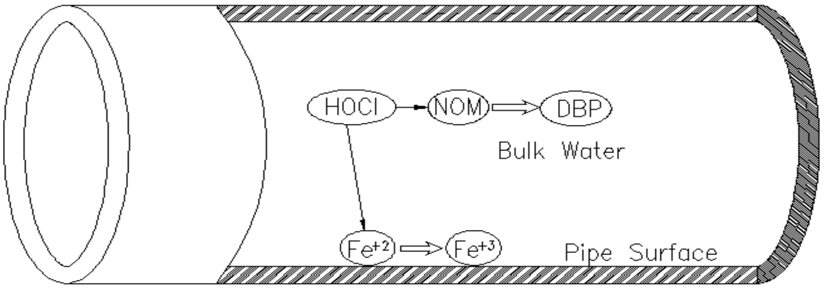


Fig.10.1. : Example of the bulk and wall reactions between chlorine and other species throughout a pipe

10.2.1. Chlorine Decay and TTHM Formation Modelling for the Bulk Phase

Traditionally, first order kinetics was used to model chlorine decay in bulk water. According to this model, chlorine concentration is assumed to decrease over time by itself. The model does not take into account other species with which chlorine reacts. The general first order kinetic expressions for chlorine decay in bulk water would be expressed as follows:

$$\frac{dC_{Cl}}{dt} = -k * C_{Cl} \qquad (10.1)$$

$$Cl(t) = Cl_0 \exp(-kt) \qquad (10.2)$$

where C_{Cl} is chlorine concentration at time t, Cl_0 is initial chlorine concentration [mg/L] and k is the decay constant [h-1].

Despite the simplicity and easiness of this model, it has not presented a good data fitting in different applications (Jabari Kohpaei and Sathasivan, 2010a; Kastl et al., 1999).

Clark (1998) proposed a two-component second-order chlorine decay model (SOM) for the prediction of chlorine decay in bulk water. The model is based on the concept of reaction between chlorine and another notional substance assuming that the balanced reaction equation could be represented as follows:

$$\mathrm{aA + bB \rightarrow pP} \tag{10.3}$$

where A and B are reacting substances; A stands for chlorine and B is a summation of all individual organic and inorganic species which potentially react with chlorine. P represents the product of the reaction.

Based on the mass balance of Equation 3 and its resulted differential equations, Clark (1998) derived an analytical solution for the second order model (SOM). The proposed solution was the first prosperous trial for SOM:

$$\mathrm{C_A = \frac{K}{1 - Re^{-ut}}} \tag{10.4}$$

where $\mathrm{C_A}$ [mg/L] is the initial chlorine concentration and K [mg/L] , R [dimensionless] and u [h-1] is constant parameters to be estimated.

Based on Equation 10.3 and assuming a liner relationship between chlorine concentration and TTHM formation at time t, Clark (1998) developed a simple formula for TTHM formation as a function of chlorine demand:

$$\mathrm{TTHM\ (t) = T\ \left(C_{Cl_0} - C_{Cl}(t)\right)} \tag{10.5}$$

where $\mathrm{C_{Cl_0}}$ and $\mathrm{C_{Cl}(t)}$ [mg/L] are the chlorine concentration at time zero and t respectively and T is a dimensionless parameter which is called TTHM yield (the amount of TTHM produced per 1 mg/L of chlorine consumption)

Kastl et al. (1999) proposed a parallel second order model (PSOM) for the entire reaction time of a typical distribution system (up to 7 days). They considered two parallel simultaneous reactions occurring between chlorine and two notional constituents in the water with the overall second order kinetics, assuming that one of the reactions is much faster than the other:

$$\mathrm{Cl_2 + FRA \xrightarrow{k_{FRA}} Cl^- + inert\ product} \tag{10.6}$$

$$\mathrm{Cl_2 + SRA \xrightarrow{k_{SRA}} Cl^- + inert\ product} \tag{10.7}$$

where FRA and SRA stand for Fast reacting Reducing Agents and Slow reacting Reducing Agents in the water respectively. $\mathrm{k_{FRA}}$ and $\mathrm{k_{SRA}}$ [mgL-1h-1] are the rate constants of the mentioned reactions. The second order reaction rates for the above-mentioned reactions in this model could be given as follows:

$$\frac{dC_{FRA}}{dt} = -k_{FRA} * C_{Cl} * FRA \tag{10.8}$$

$$\frac{dC_{SRA}}{dt} = -k_{SRA} * C_{Cl} * SRA \tag{10.9}$$

where C_{FRA} and C_{SRA} [mg/L] are concentration of the two reacting agents (fast and slow), respectively.

$$\frac{dC_{Cl}}{dt} = \frac{dC_{FRA}}{dt} + \frac{dC_{SRA}}{dt} \tag{10.10}$$

where C_{Cl} [mg/L] is free chlorine concentration.

Assuming that $\propto = \frac{k_{SRA}}{k_{FRA}}$ is considerably low, which is a true assumption according to the literature, Jabari Kohpaei and Sathasivan (2010b) proposed an analytical solution for the parallel second order model as follows:

$$C_{Cl_{FRA}}(t) = \frac{a-b}{1-\frac{b}{a}e^{-(a-b)k_{FRA}t}} \tag{10.11}$$

$$C_{Cl}(t) = \frac{C_{Cl_{FRA}}(t) - c}{1 - \frac{c}{C_{Cl_{FRA}}(t)} e^{-\left(C_{Cl_{FRA}}(t)-c\right)k_{SRA}t}} \tag{10.12}$$

where $a = C_{Cl_0}$ [mg/L] is the initial chlorine concentration and $b = C_{FRA_0}$ and $c = C_{SRA_0}$ [mg/L] are the initial concentrations of FRA and SRA, respectively.

10.2.2. Incorporation of the Wall Reaction (Surface Phase)

EPANET (Rossman, 2000) allows specification of surface decay reaction according to the following equation:

$$\frac{dC_{Cl}}{dt} = -\left({}^{A}\!/_{V}\right) * K_w * C_{Cl}^n \tag{10.13}$$

where ${}^{A}\!/_{V}$ (equal to 4 divided by the diameter) is surface area per unit of volume, K_w is the wall reaction coefficient and n is the order of reaction limited to 0 or 1. Based on the reaction order being used (n=zero or 1), the units of K_w are either mass/area/time or length/time, respectively.

10.3. Water Samples and Analytical Methods

The water sample taken from Pilbara Water Treatment Plant effluent, labelled as “Pilbara Post-Filtration Water (PPFW_35)”, was used for the tests. Prepared chlorine-demand-free amber bottles were used to store the water sample. Table 1 presents the water quality characteristics of the sample used in authors’ experiments. Considering the average temperature of the region of nominated distribution system, the sample was examined at the temperature of 35˚C. The water sample was dosed at three different chlorine concentrations with the lowest selected to produce a residual concentration near zero (3.2mg/L, 5.4mg/L and 8.4mg/L). The highest chlorine concentration was selected to produce an appropriate range to cover the whole variation of the chlorine concentration within the system.

All chlorine measurements were conducted with the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method using Lovibond pocket colorimeters. To minimise the effects of variations in the water quality, repeated tests were done and the results were compared for consistency. Diluted standard sodium hypochlorite solution was used for chlorination of the samples. Several experiments with de-ionized water were conducted before the main tests to confirm the initial chlorine concentrations. Before beginning any sampling for the experiments, all involving containers and glassware were cleaned with de-ionized water to ensure that no chlorine demand was present. Duplicate analysis was performed on each sample, and the average was reported. If the difference between the two values was greater than 10%, a third analysis was performed, and the average of all three values was reported.

Table.10.1 : Water Quality Characteristics of the Sample

Data source	Sample label	Water quality characteristics		
		DOC (mgL-1)	UV254 (cm-1)	pH
Pilbara Post-Filtration Water	PPFW	2.43	0.024	7.78

10.4. Parameter Estimation

Data obtained from the tests were classified into different categories according to their initial chlorine concentration. In order to consider the variation in chlorine dosing, only one set of parameters was allocated to all data of the water sample with different initial chlorine concentrations.

Employing the previously explained parallel second order modelling method (PSOM), data analysis was performed using AQUASIM (Reichert 1994). The data of free chlorine readings from the laboratory experiments were put into one file to be run in AQUASIM software. In this file, four program parameters (CFRA0, CSRA0, kFRA and kSRA) and two reaction schemes (fast and slow) were defined for the data set.

Since the parallel second order model was provided with an analytical solution, using a useful Excel application for data fitting, called “Excel Solver”, the data fitting procedure was performed using the proposed analytical solution. With this method of analysis, apart from comparing the results of analytical and numerical solution, more statistical measures such as R-square and SSE (Sum of Squares due to Errors) for the assessment of the correlation between predicted and measured data values were obtained. SSE is a statistical parameter, which measures the total deviation of the response values from the fit to the measured data values.

10.5. Brief Description of the Pilot Water Distribution System

The nominated water supply system supplies water to the main towns of a township area in the north-west of Western Australia including the towns of KA, DA, RO and WI (acronyms have been used instead of full names of the towns). There are two main water sources to meet the drinking water demand of the region: HA Dam (surface water) and/or MI Aquifer (groundwater). The MI Aquifer is the secondary source and is used only when water is not available for supply from the HA Dam. Figure 10.2 illustrates a general layout of the nominated water distribution system when it is sourced from HA Dam only. According to Figure 10.2, when the network is supplied from HA Dam, water is pumped from the treatment plant through two different lines: one pipeline pumps water to the PL Tank near the dam area and another pipeline sends water to the YA Tank in another location. From PL Tank, water gravitates to KA Tanks. Also, throughout different route, i.e. CL pipeline, the water is transferred to the CL Tank. The CL pipeline supplies water to the tanks at RO, WI and CL townships. YA Tank supplies water to DA Tanks by gravity.

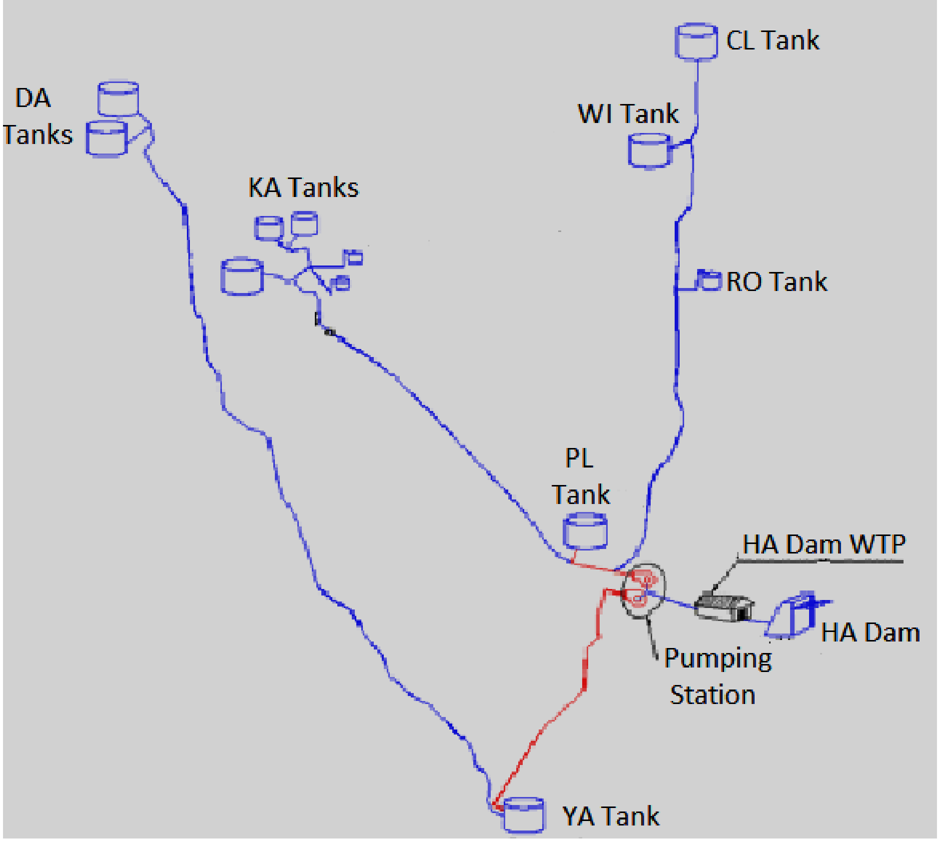


Fig.10.2. General layout of the Pilot Water Distribution System

10.6. Hydraulic Modelling Procedure:

For modelling chlorine decay for any distribution system, first, hydraulic model of the system should be implemented. EPANET software (Rossman, 2000) was used to simulate the network and to conduct the hydraulic modelling of the distribution system. After obtaining necessary parameters from laboratory experiments, the first step for modelling chlorine decay and DBPs formation in the distribution system is to establish the hydraulic model of the system.

10.6.1. Geometry of the Model:

Information about the geometry of the distribution system, such as pipe material, diameter and length, elevations of the tanks and important joints, etc., was obtained from the existing design drawings and documents and by on-site inspection. Figure 10.3 presents a schematic geometry of the pilot water distribution system.

10.6.2. Hydraulic Information and Calibration:

Hydraulic information of the distribution system, such as demands of the destinations and the conditions of the pumps and water tanks, was obtained from the database linked to the on-line monitoring system of the network. However, because hydraulics of the real system was so complicated, it was attempted to simplify the system by using equivalent options. For example, in the real system, a pipeline may be used for both pumping water to a tank and also for gravity feeding a destination from the same tank when the pump was offline. To simplify the system in EPANET, one pipe was used for pumping water into the tank and another pipe, with the same properties, was used for gravity feeding from the tank.

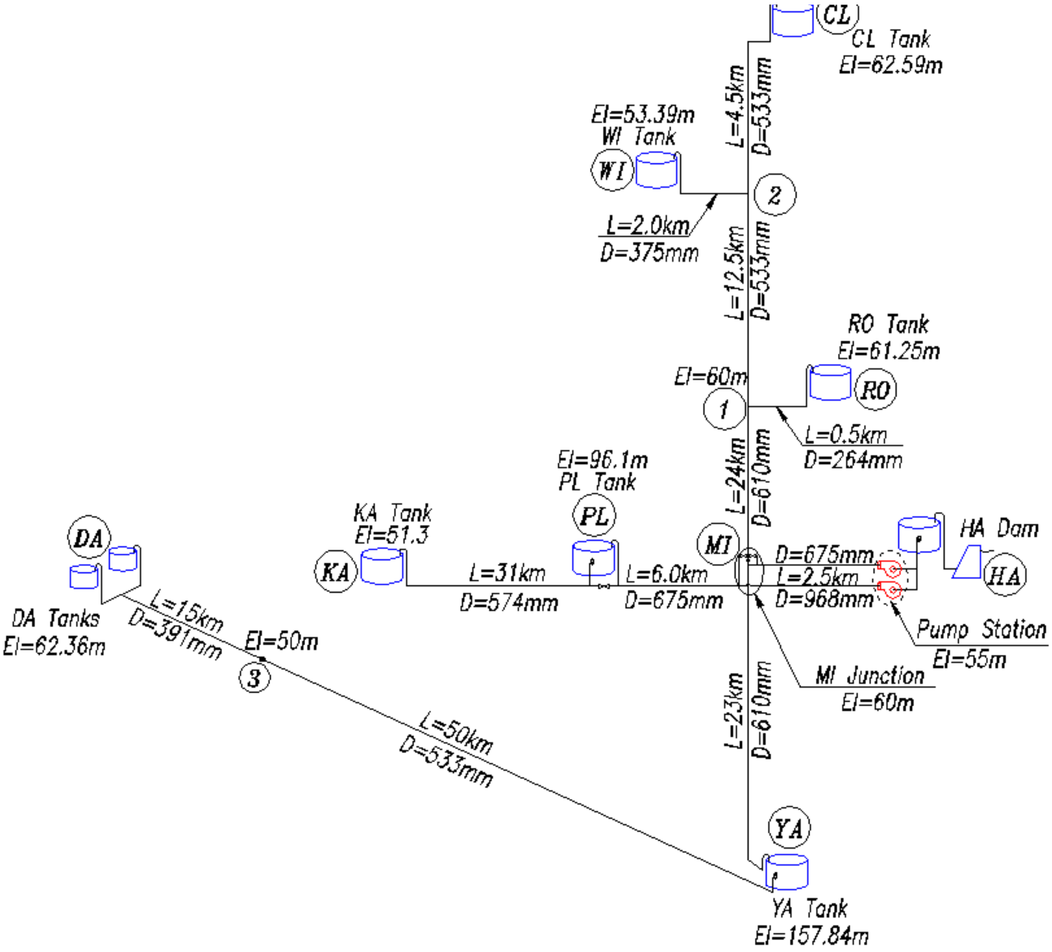
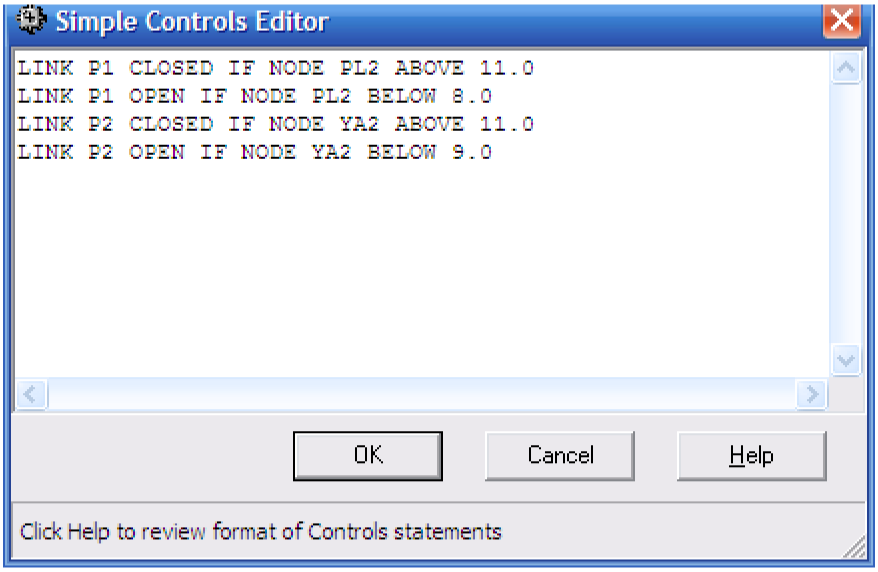


Fig.10.3. : Schematic geometry of the pilot water distribution system

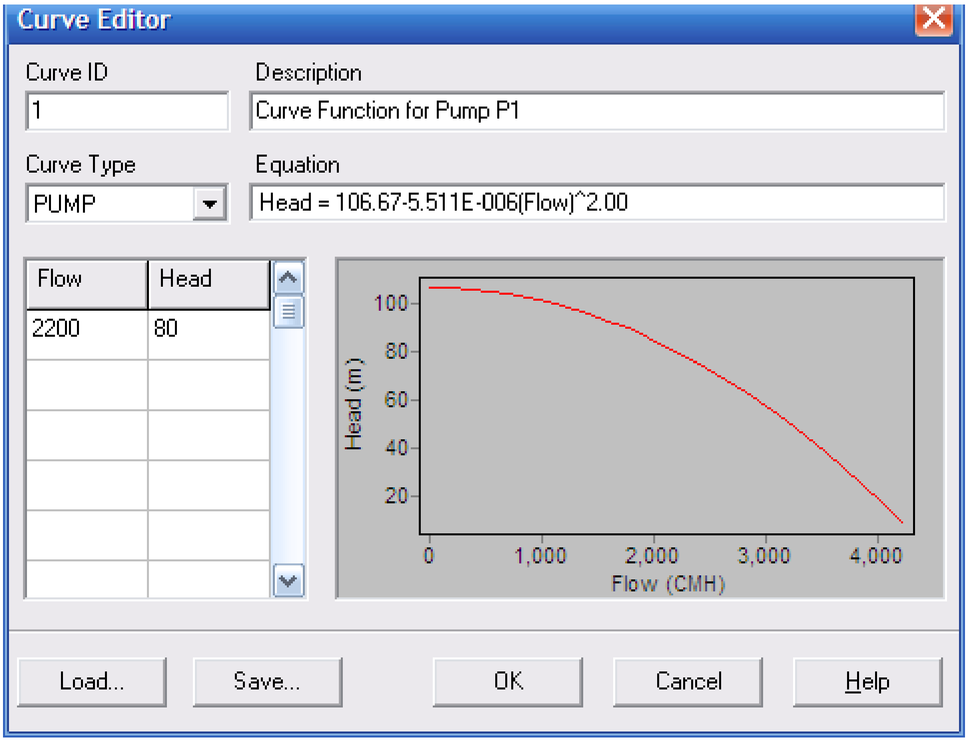
In order to simulate the conditions of the pumps, as it was found difficult to find a constant trend, simple controls in EPANET were used to control the pumps according to the level of their target tanks. In addition, each pump was given a curve function that could produce the same hydraulic situation (flow rate and pressure before and after the pump) as it does in the real system. Figure 10.4 shows the syntax of the simple controls that were applied to the model and Figures 10.5 and 10.6 illustrate the curve functions of the pumps.



```
LINK P1 CLOSED IF NODE PL2 ABOVE 11.0
LINK P1 OPEN IF NODE PL2 BELOW 8.0
LINK P2 CLOSED IF NODE YA2 ABOVE 11.0
LINK P2 OPEN IF NODE YA2 BELOW 9.0
```

Click Help to review format of Controls statements

Fig.10.4.: The syntax of the Simple Controls for the pumps P1 and P2



Curve ID: 1

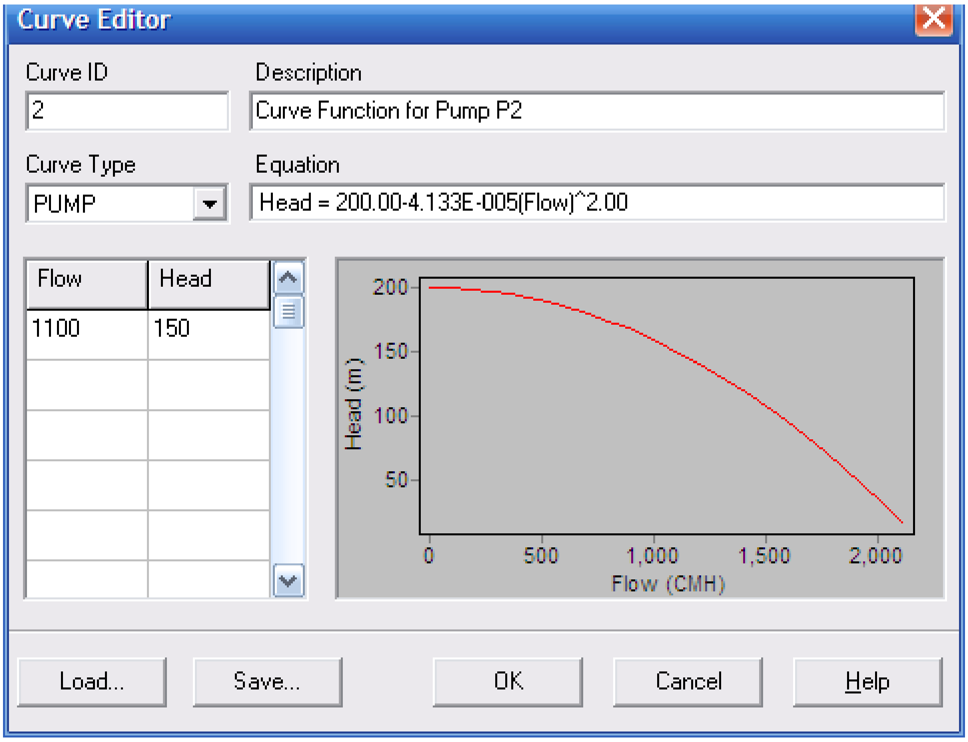
Description: Curve Function for Pump P1

Curve Type: PUMP

Equation: Head = 106.67-5.511E-006(Flow)^2.00

Flow	Head
2200	80

Fig.10.5.: The Curve function for the pump P1



Curve ID: 2

Description: Curve Function for Pump P2

Curve Type: PUMP

Equation: Head = 200.00-4.133E-005(Flow)^2.00

Flow	Head
1100	150

Fig.10.6. : The Curve function for the pump P2

To determine a demand pattern, which is close to real on-site measurements, initially, a long period (about 6 months) of the actual on-site measured flow rates after WI Tank and KA Tank was collected and studied. The average, maximum and minimum values of the demand for a represented 24-hour period were determined. Based on that, a 24-hour demand pattern was generated and evaluated against the real data. Figure 10.7 shows the on-site measured flow rates after WI Tank between 31/08/2009 and 29/03/2010. Figure 10.8 presents the same data for a shorter period between 07/10/2009 and 14/10/2009. Figures 10.9 illustrates the demand pattern no.1, which was calculated based on the recorded flow rates after WI Tank. As there was not enough information about the water demand of RO and CL and assuming that the demand trend for these towns is mostly residential and similar to WI, the previously calculated pattern was considered for RO and CL as well. Figures 10.10 and 10.11 show the generated flow rates after WI tank for a period of 7 days and 6 months respectively.

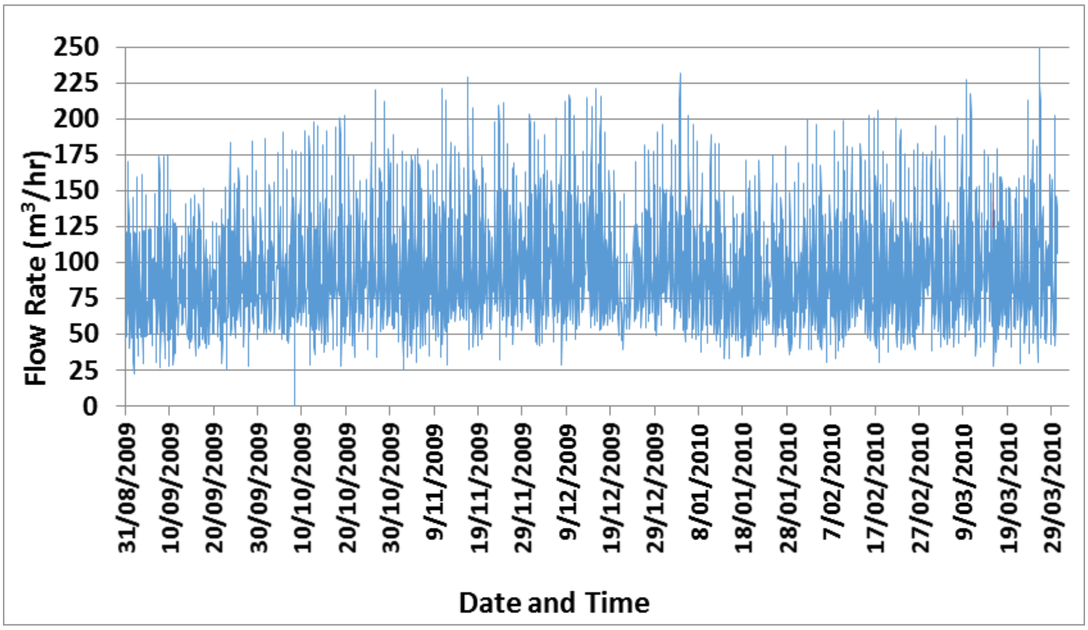


Fig.10.7.: On-site measured flow rates (m3/hr) after WI Tank between 31/08/2009 and 29/03/2010

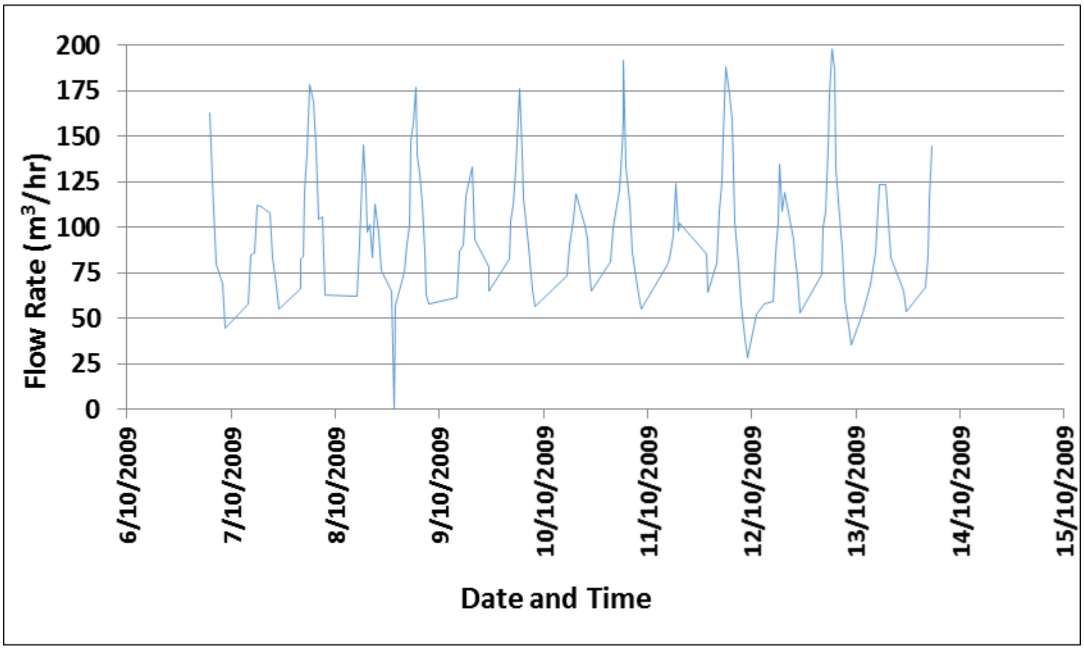
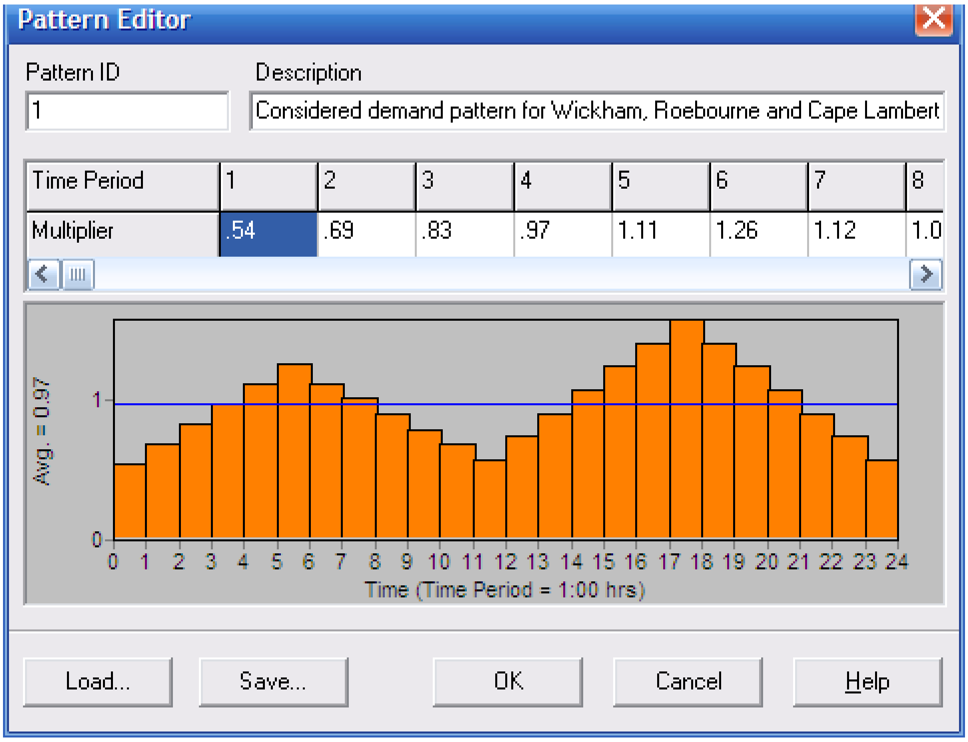


Fig.10.8.: On-site measured flow rates (m3/hr) after WI Tank between 07/10/2009 and 14/10/2009



Pattern ID: 1

Description: Considered demand pattern for Wickham, Roebourne and Cape Lambert

Time Period	1	2	3	4	5	6	7	8
Multiplier	.54	.69	.83	.97	1.11	1.26	1.12	1.0

Fig.10.9. : Demand pattern no.1 considered for WI, RO and CL

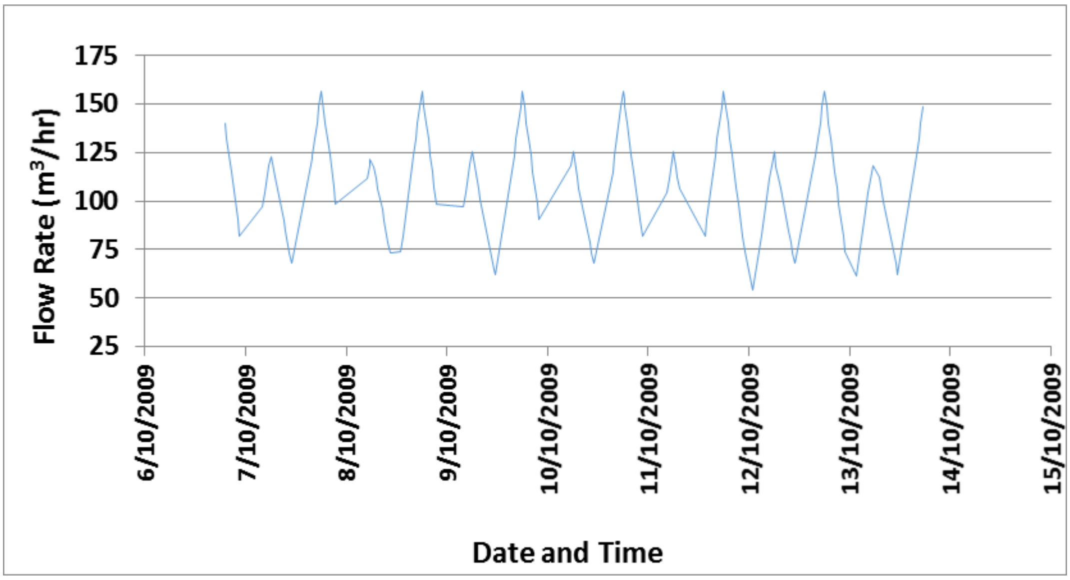


Fig.10.10. : Built-up flow rates (m3/hr) after WI Tank between 07/10/2009 and 14/10/2009 based on pattern no.1

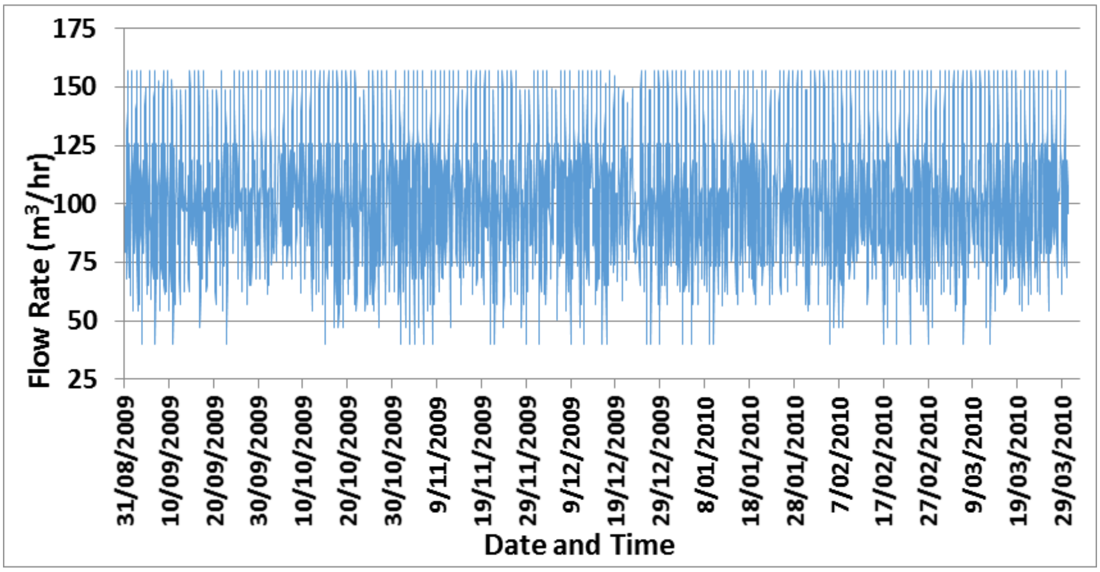


Fig.10.11. : Built-up flow rates (m3/hr) after WI Tank between 31/08/2009 and 29/03/2010 based on pattern no.1

Similarly, Figures 10.12 to 10.16 show the procedure for the calculation of the demand for KA and DA. It should be noticed that similar to what is mentioned before, because of lack of information for DA, the calculated demand pattern for KA, as an industrial, commercial and residential area, was considered for DA as well.

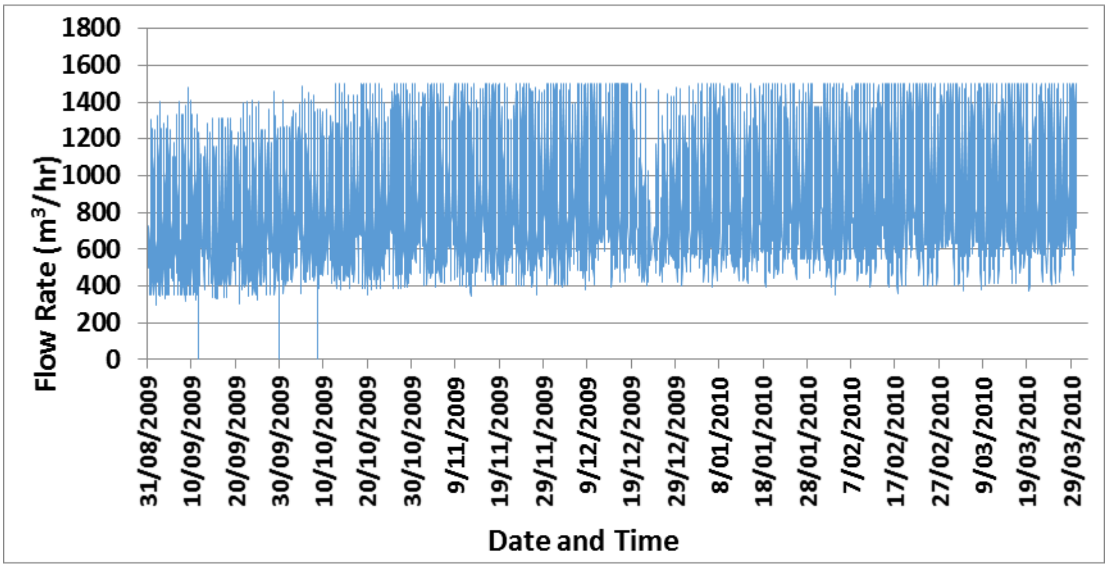


Fig.10.12. : On-site measured flow rates (m3/hr) after KA Tank No.3 between 31/08/2009 and 29/03/2010

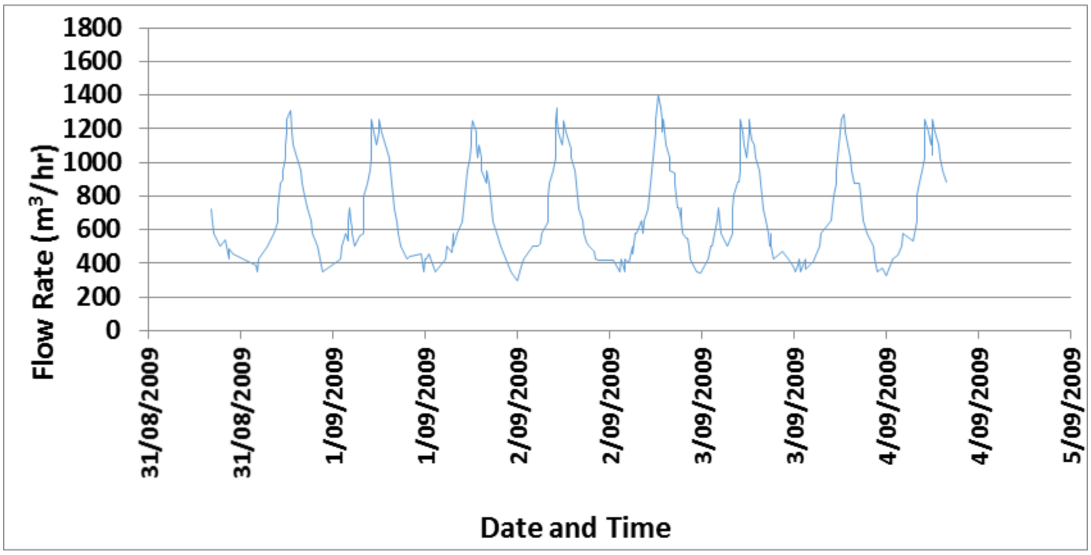
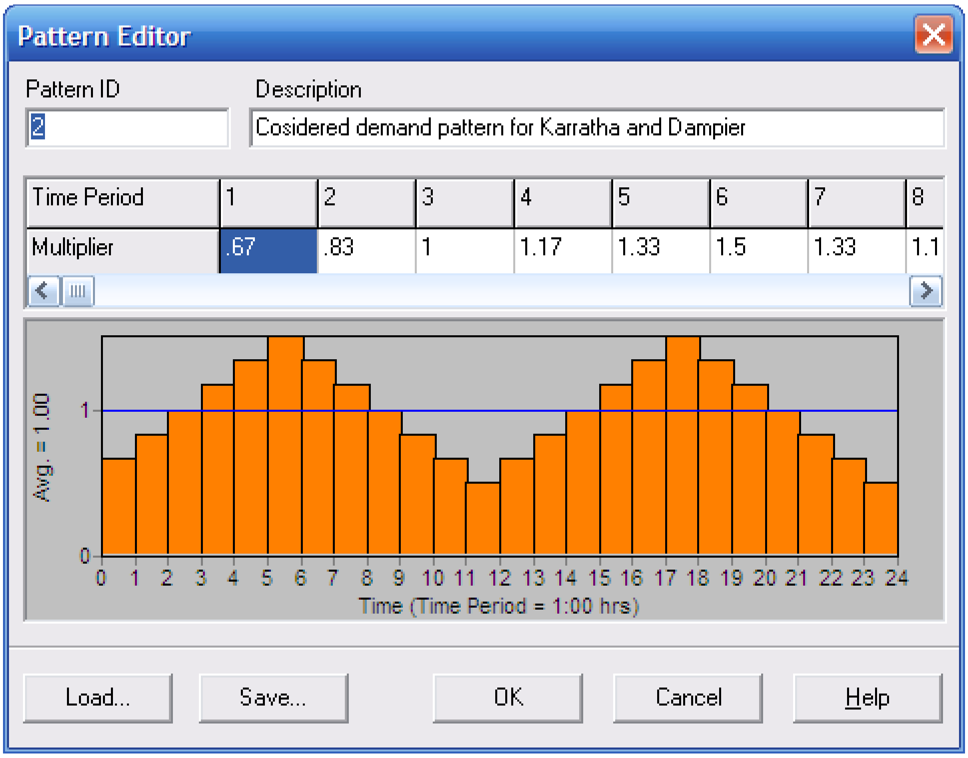


Fig.10.13. : On-site measured flow rates (m3/hr) after KA Tank No.3 between 31/08/2009 and 4/09/2009



Pattern ID: 2

Description: Cosidered demand pattern for Karratha and Dampier

Time Period	1	2	3	4	5	6	7	8
Multiplier	.67	.83	1	1.17	1.33	1.5	1.33	1.1

Fig.10.14. : Demand pattern no.2 considered for KA and DA

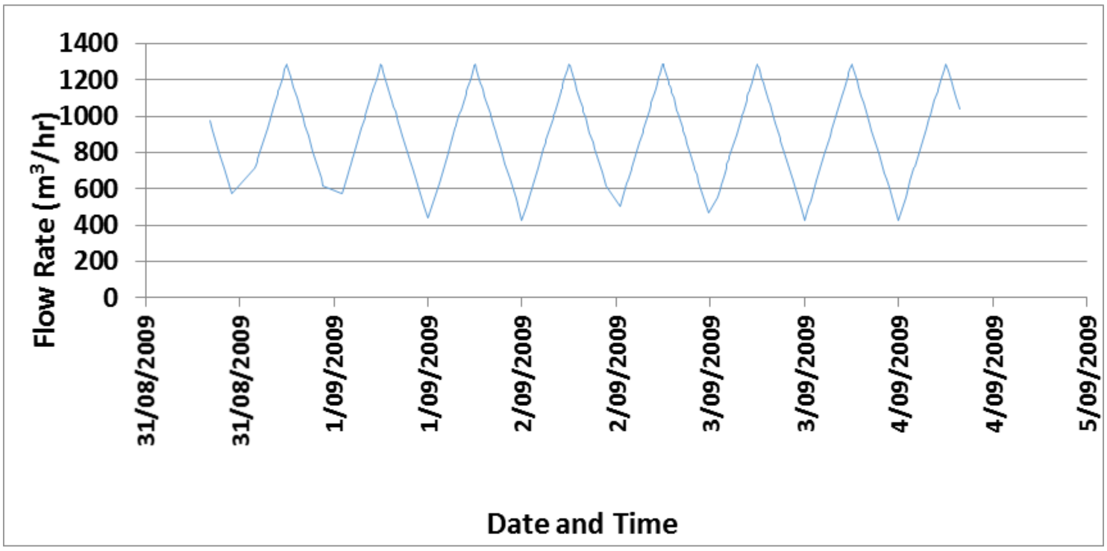


Fig.10.15. : Built-up flow rates (m3/hr) after KA Tank No.3 between 31/08/2009 and 04/09/2009 based on pattern no.2

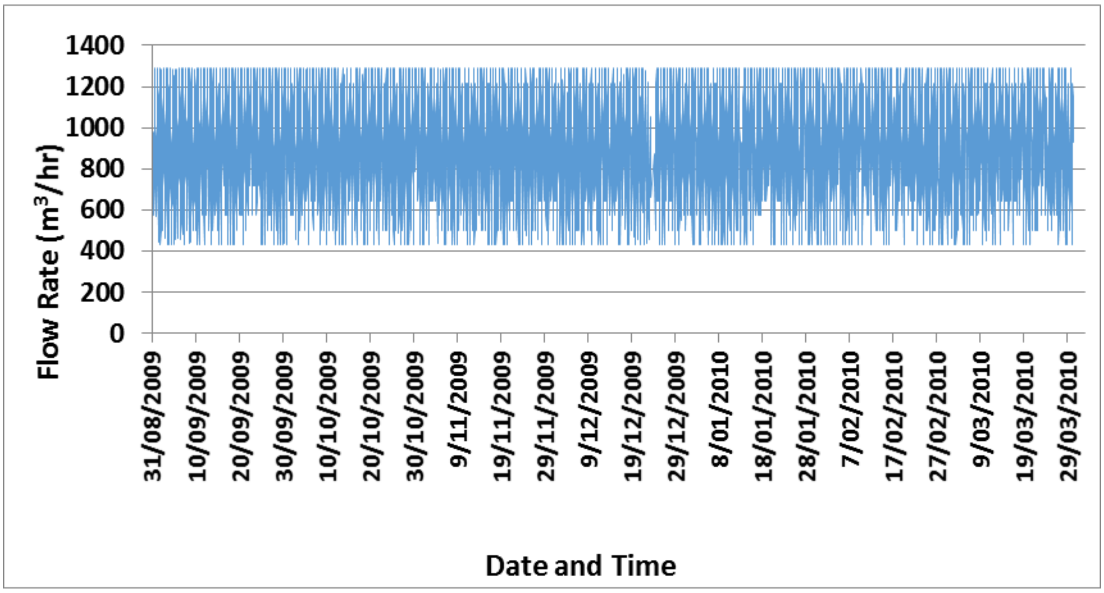


Fig.10.16. : Built-up flow rates (m3/hr) after KA Tank No.3 between 31/08/2009 and 29/03/2010 based on pattern no.2

The following have been considered for undertaking the hydraulic modelling of the distribution system.

- For each tank, two extra joints were defined; one is immediately before and one is after the tank. The reason behind is to observe the chlorine decay and DBPs formation before and after the mixing process inside the tank.
- For some pipes, such as the one take water to RO tank, check valves were applied in order to control the direction of the flow within those pipes.

- The maximum level of the tanks was assigned according to the operational information. An appropriate initial water level for each tank was considered to remove the chance of getting warning of negative pressure for upstream during the initial hours of the simulation.
- A total period of 240 hours considered as the simulation time to maintain the consistency of the hydraulic and quality situation of the system.

Figure 10.17 illustrates a general view of the hydraulic model in EPANET. Figure 10.18 shows the flow rate in each pipe after 90 hours from the beginning the simulation.

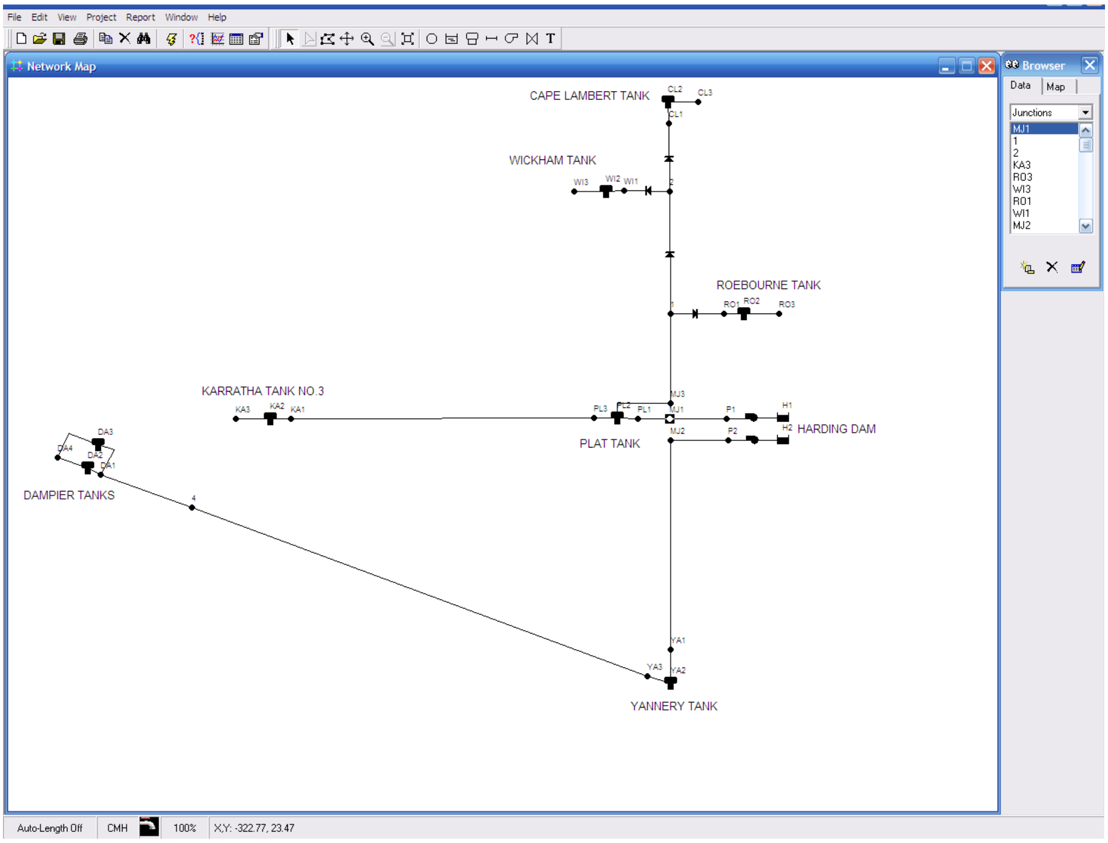


Fig.10.17. : General outline of hydraulic model in EPANET

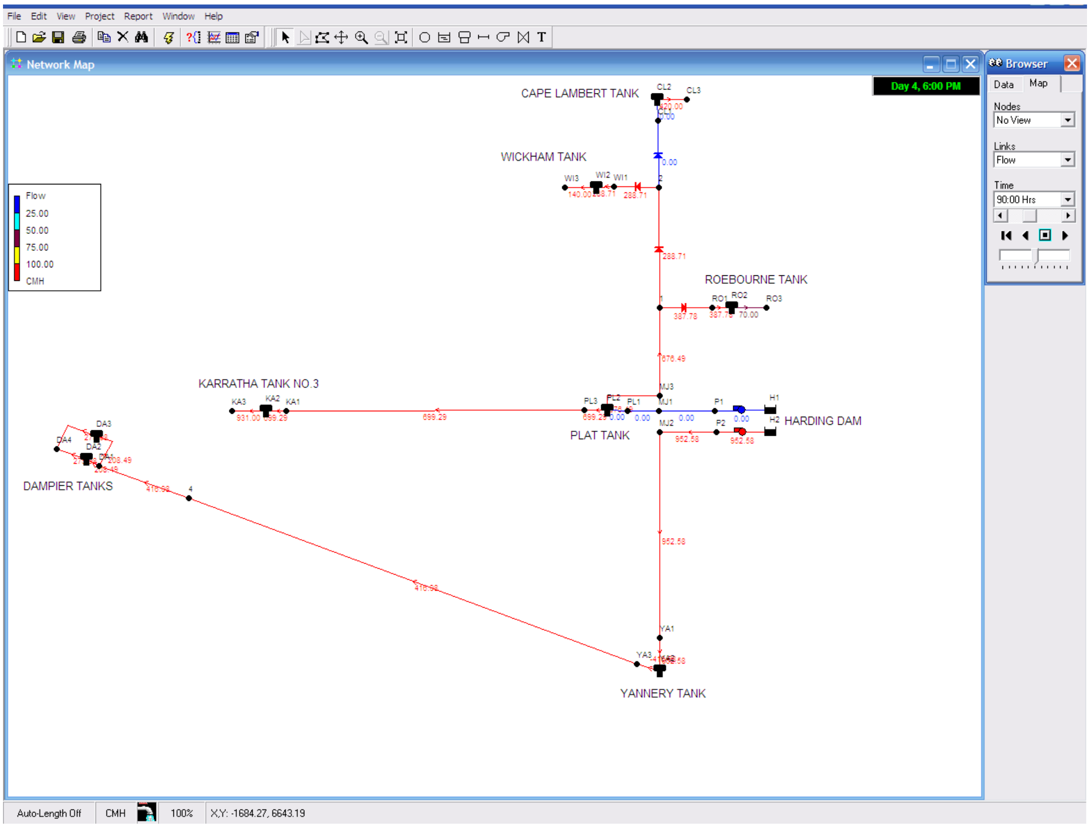


Fig.10.18. : Flow rates in the pipes at time 90hr

10.7. Water Quality Modelling Procedure:

To model the chlorine decay and DBPs formation, EPANET-MSX (Shang et al., 2008) software was used. EPANET-MSX, where MSX stands for Multi-Species Extension, is an extension to the original EPANET that allows it to model any system of multiple, interacting chemical species.

The second step in running a multi-species analysis of the water distribution system, after preparing the standard EPANET input file, is to prepare the MSX input file that defines the individual water quality species of interest and the reaction expressions that govern their dynamics.

Assuming the average temperature of the pilot area/region to be 35˚C, the results of parameter estimation related to this temperature were used for the simulation. However, it would be easy to change the input file to perform the model for temperatures rather than 35 and it is enough to change the parameters’ values to the ones obtained from new conditions (temperature).

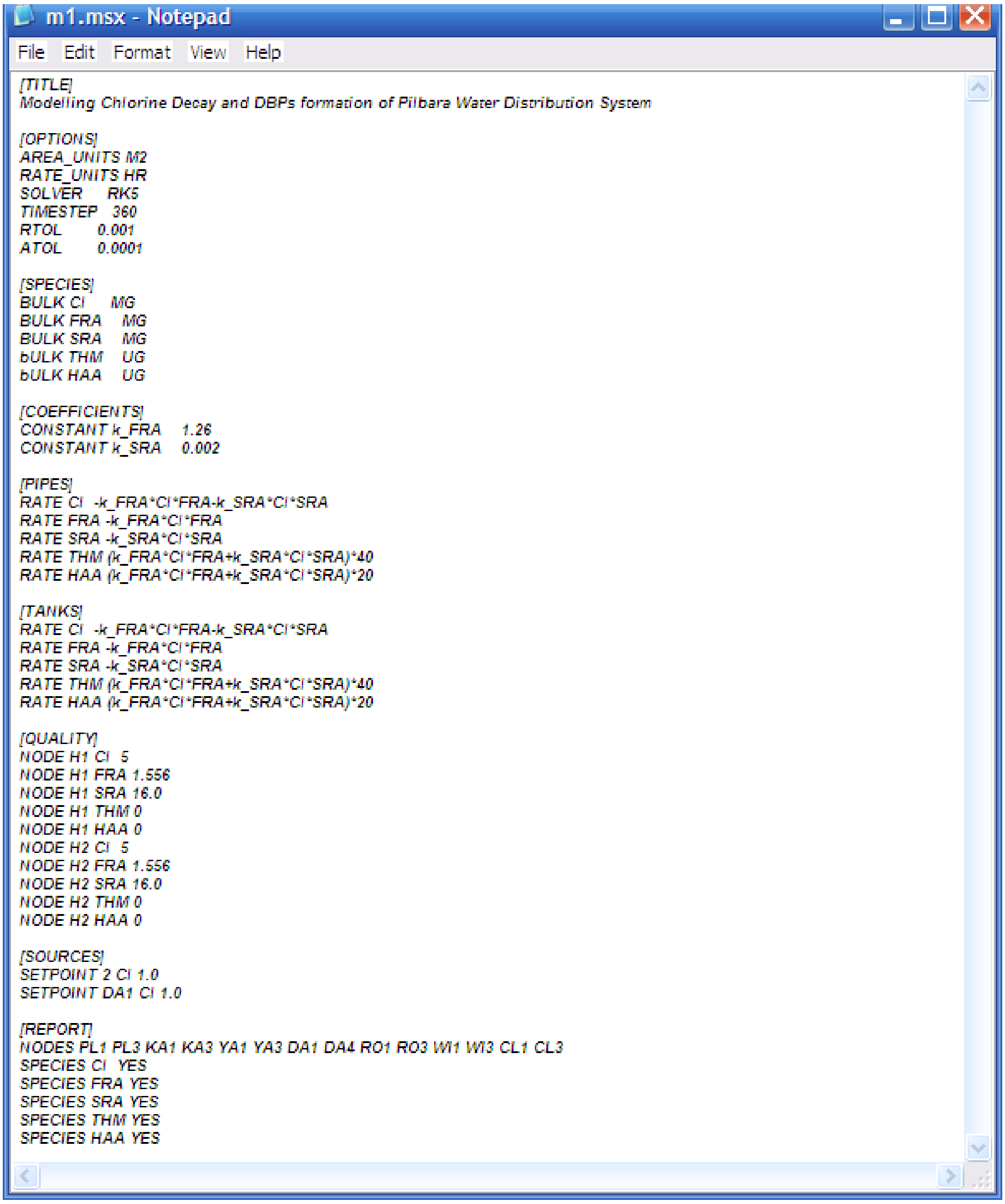
As enough DBPs (THM and HAA) analysis has not been conducted, to calculate the amount of DBPs to be formed, the yield values from previous experiments were used.

According to those results, for 1 mg/L of chlorine demand 40 μg/L of THM and 20 μg/L of HAA were considered to be formed within the system.

In order to model rechlorination scenario, a set point value of 1 mg/L was maintained for joints 2 (before WI Tank) and also for joint DA1 (before DA Tanks).

10.7.1. MSX Input File:

Figure 10.19 shows the outline of the EPANET-MSX input file that was written for the modelling of chlorine decay and DBPs formation of the pilot water distribution system.



```
[TITLE]
Modelling Chlorine Decay and DBPs formation of Pilbara Water Distribution System

[OPTIONS]
AREA_UNITS M2
RATE_UNITS HR
SOLVER     RK5
TIMESTEP   360
RTOL       0.001
ATOL       0.0001

[SPECIES]
BULK Cl     MG
BULK FRA    MG
BULK SRA    MG
bULK THM    UG
bULK HAA    UG

[COEFFICIENTS]
CONSTANT k_FRA    1.26
CONSTANT k_SRA    0.002

[PIPES]
RATE Cl  -k_FRA*Cl*FRA-k_SRA*Cl*SRA
RATE FRA -k_FRA*Cl*FRA
RATE SRA -k_SRA*Cl*SRA
RATE THM (k_FRA*Cl*FRA+k_SRA*Cl*SRA)*40
RATE HAA (k_FRA*Cl*FRA+k_SRA*Cl*SRA)*20

[TANKS]
RATE Cl  -k_FRA*Cl*FRA-k_SRA*Cl*SRA
RATE FRA -k_FRA*Cl*FRA
RATE SRA -k_SRA*Cl*SRA
RATE THM (k_FRA*Cl*FRA+k_SRA*Cl*SRA)*40
RATE HAA (k_FRA*Cl*FRA+k_SRA*Cl*SRA)*20

[QUALITY]
NODE H1 Cl  5
NODE H1 FRA 1.556
NODE H1 SRA 16.0
NODE H1 THM 0
NODE H1 HAA 0
NODE H2 Cl  5
NODE H2 FRA 1.556
NODE H2 SRA 16.0
NODE H2 THM 0
NODE H2 HAA 0

[SOURCES]
SETPOINT 2 Cl 1.0
SETPOINT DA1 Cl 1.0

[REPORT]
NODES PL1 PL3 KA1 KA3 YA1 YA3 DA1 DA4 RO1 RO3 WI1 WI3 CL1 CL3
SPECIES Cl  YES
SPECIES FRA YES
SPECIES SRA YES
SPECIES THM YES
SPECIES HAA YES
```

Fig.10.19. : Input MSX file for modelling chlorine decay and DPBs formation within the pilot distribution system

10.8. Results and Discussions

The results of parameter estimation for the data of chlorine decay test for PPFW sample from Pilbara Post-Filtration Water at 35˚C with PSOM are presented in Table 10.2. Figures 10.20 and 10.21 show the goodness of data fitting for the collected Pilbara water sample analysed with the parallel second order model (PSOM) using analytical solution via Excel Solver and numerical method with AQUASIM.

Table.10.2 Results of parameter estimation for Pilbara Post-Filtration Water sample at 35˚C

Sample name	Parameters	Parameter estimation		
		Numerical solution with parallel second order model using AQUASIM	**New analytical solution using Excel SOLVER**	**Absolute Difference**
PPFW_35	**FRA_0**	**1.556**	**1.556**	**0.000**
	SRA_0	**15.977**	**16.126**	**0.149**
	k_{FRA}	**1.253**	**1.267**	**0.014**
	k_{SRA}	**0.002**	**0.002**	**0.000**
	R^2*	**---**	**0.980**	**---**
	SSE*	**---**	**2.467**	**---**
	Chi^2*	**2.403**	**---**	**---**

*R^2: R-Square; SSE: Sum Squared Error; Chi2: Chi-Square

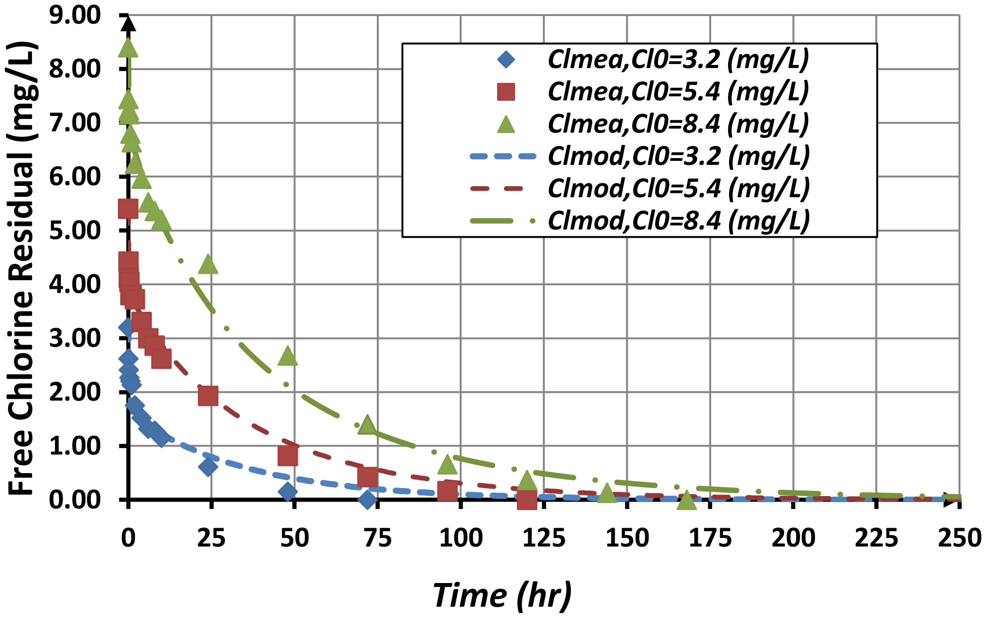


Fig.10.20. Goodness of Data fitting for the Pilbara Post Filtration Water sample data set at 35˚C using analytical solution with Excel SOLVER

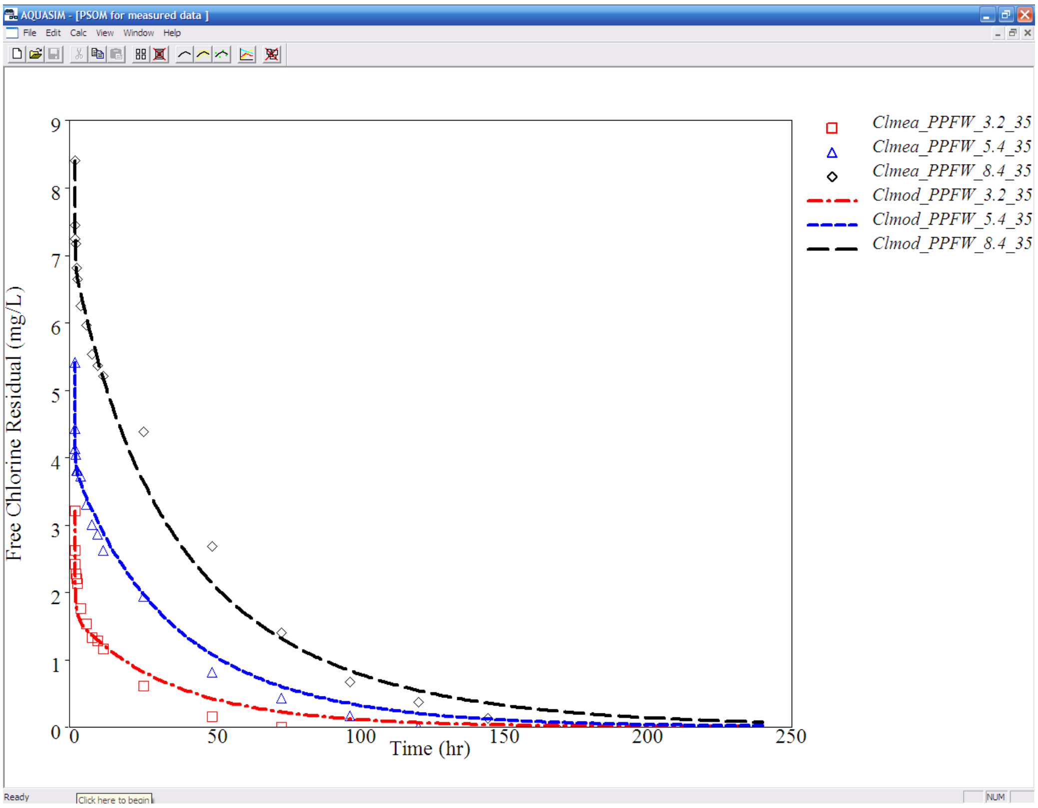


Fig.10.21. Goodness of Data fitting for the Pilbara Filtration Water sample data set at 35˚C using numerical solution with AQUASIM

As can be seen from Table 10.2, the results of parameter estimation with analytical solution is very close to the ones calculated with numerical methods. Apart from the original intention of this research, it shows the accuracy of the analytical solution and confirms that the method could be used as an alternative means for performing parameter estimation or to evaluate the results of numerical solutions.

The results of DBP tests showed that the yield of formation (T in Equation 10.5) was around 40μg/L for TTHM (total trihalomethanes) and around 20μg/L for THAA (total haloacetic acids). The results of a previous study have shown that there was no evidence of the wall reaction (biofilm or wall material) incorporated with the chlorine decay within the distribution system. Therefore, the effect of surface phase (wall reaction) was ignored in this simulation.

Figures 10.22 to 10.34 show the result of the chlorine decay simulation in the nominated pilot distribution system.

As can be seen from the figures presenting the DBPs formation, the graph showing the formation of the DBPs starts from zero and increases gradually to reach a constant level. This level should be read as the result of DBPs formation for the intended location. In some graphs (e.g. Figure 10.25), however, the DBPs formation seems to be still increasing with time. This means more simulation time may be required in order to reach a constant result.

Fluctuation in some graphs is due to the pump or demand trend or it is because the flow within some pipes may be stopped, as the maximum level in upper tank is reached.

Table 10.3 compares the results of the performed quality simulation with the average results obtained from on-site measurements. It shows a good match between predicted results from modelling process and the average values obtained from on-site measurements.

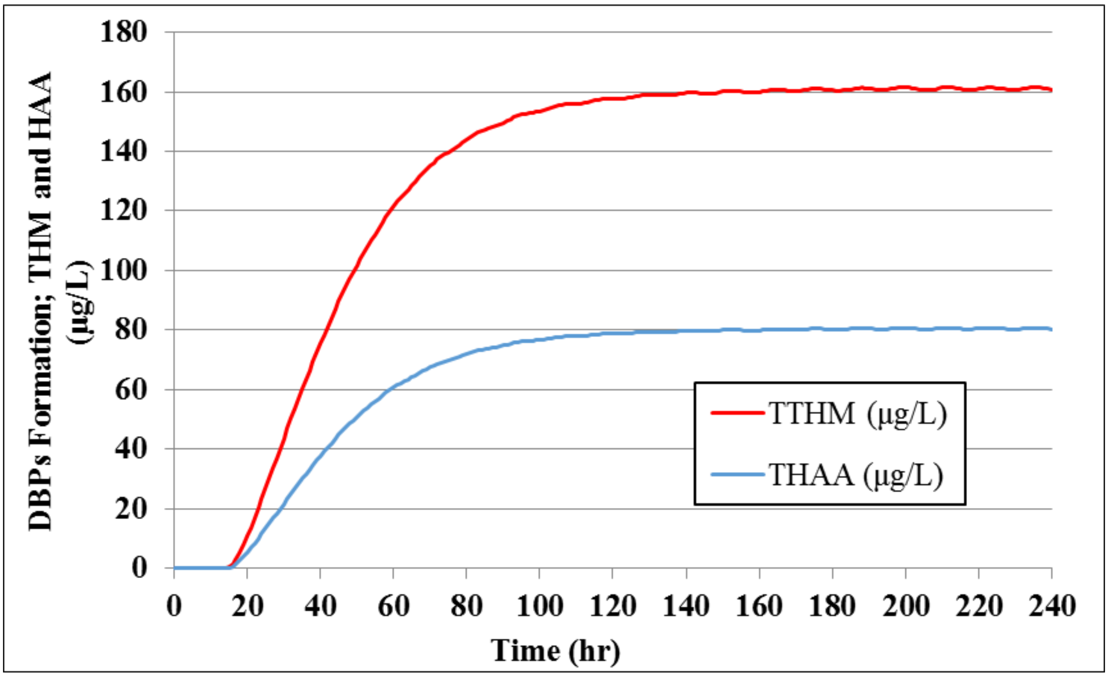


Fig.10.22. : DBPs (THM and HAA) formation at node KA3 (after KA Tank No.3)

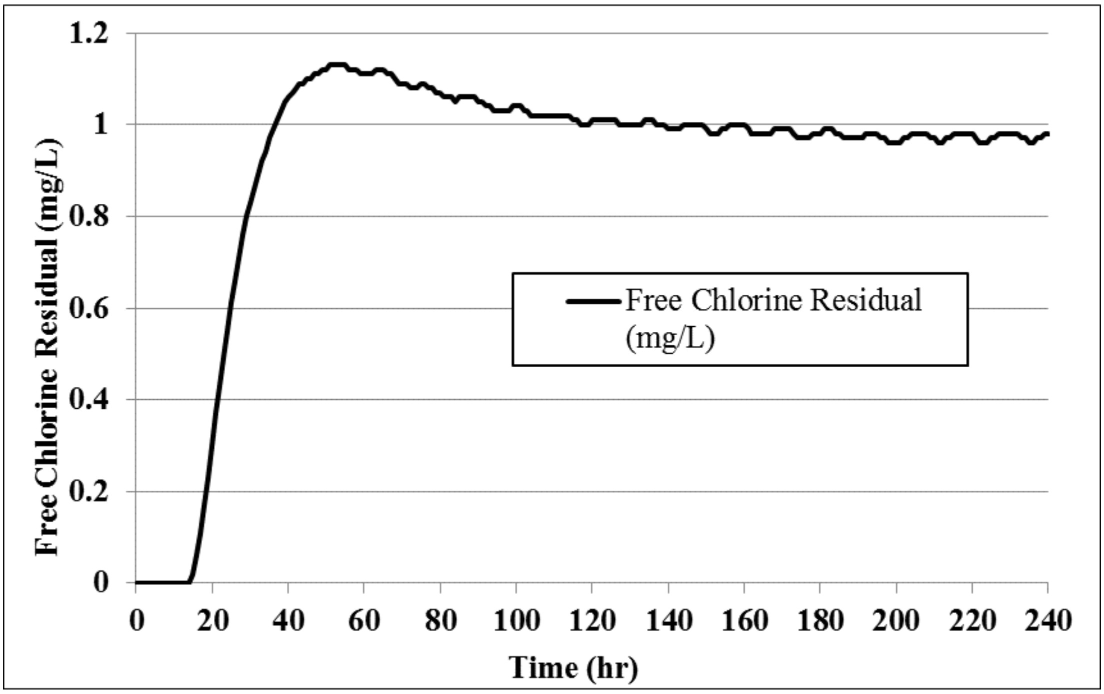


Fig.10.23. : Free chlorine residual at node KA3 (after KA Tank No.3)

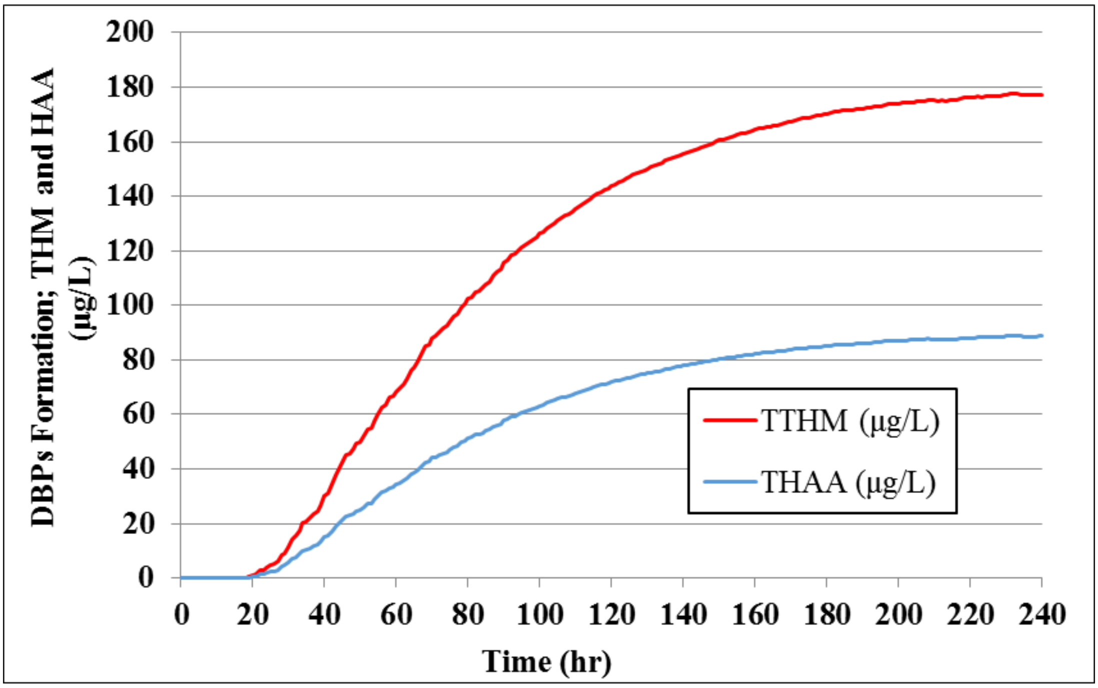


Fig.10.24. : DBPs (THM and HAA) formation at node RO3 (after RO Tank)

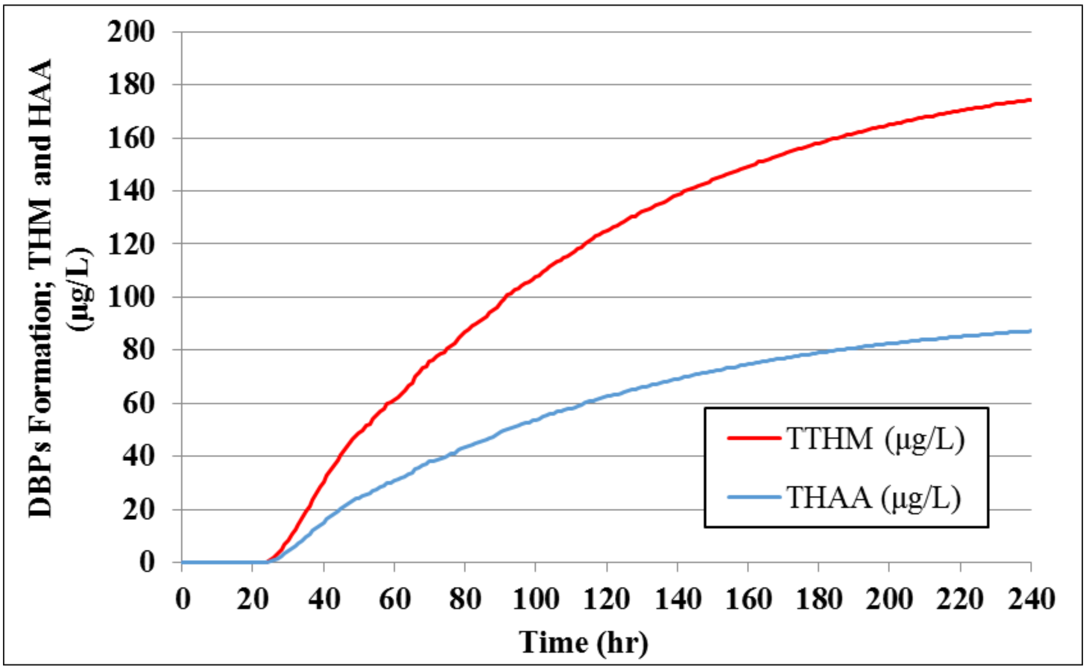


Fig.10.25. : DBPs (THM and HAA) formation at node WI3 (after WI Tank)

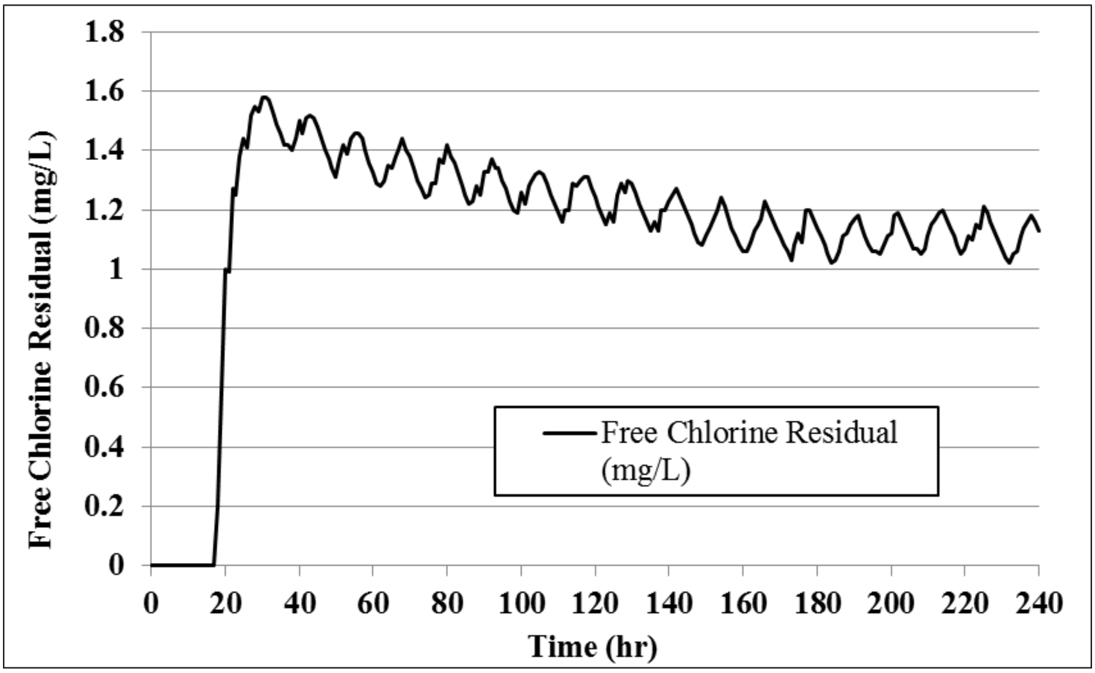


Fig.10.26. : Free chlorine residual at node RO1 (before RO Tank)

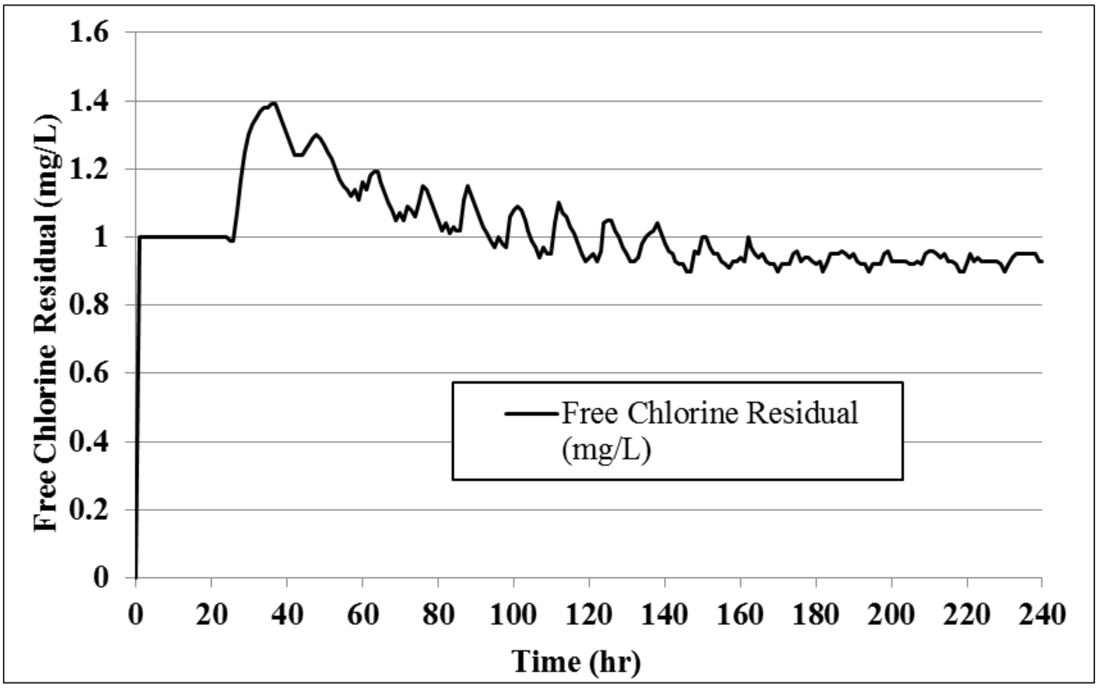


Fig.10.27. : Free chlorine residual at node WI1 (before WI Tank)

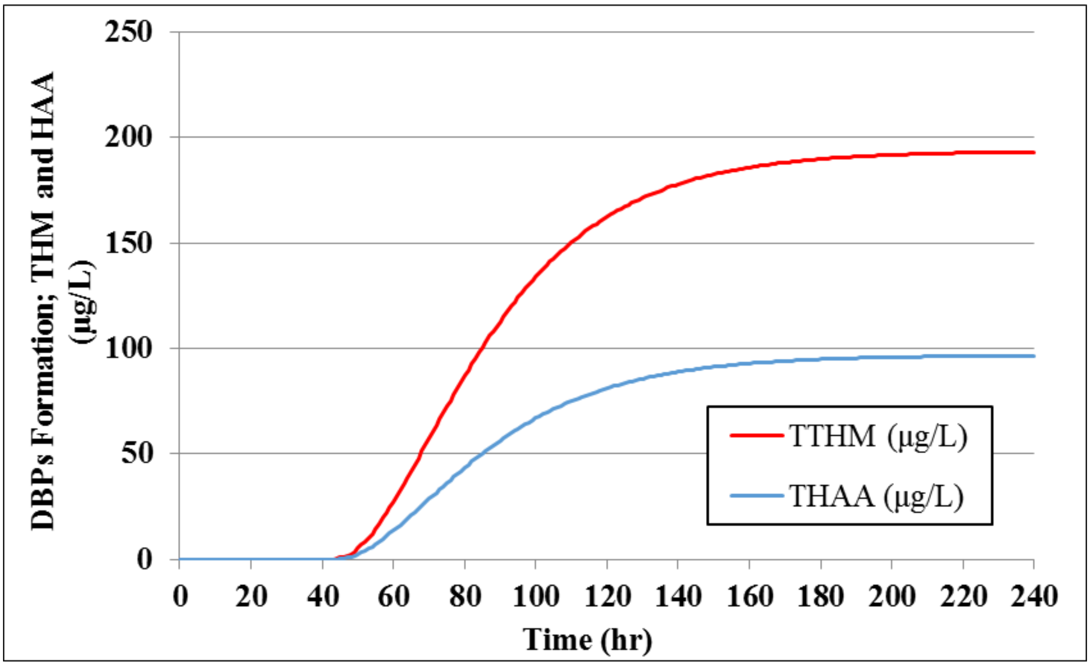


Fig.10.28. : DBPs (THM and HAA) formation at node DA4 (after DA Tanks)

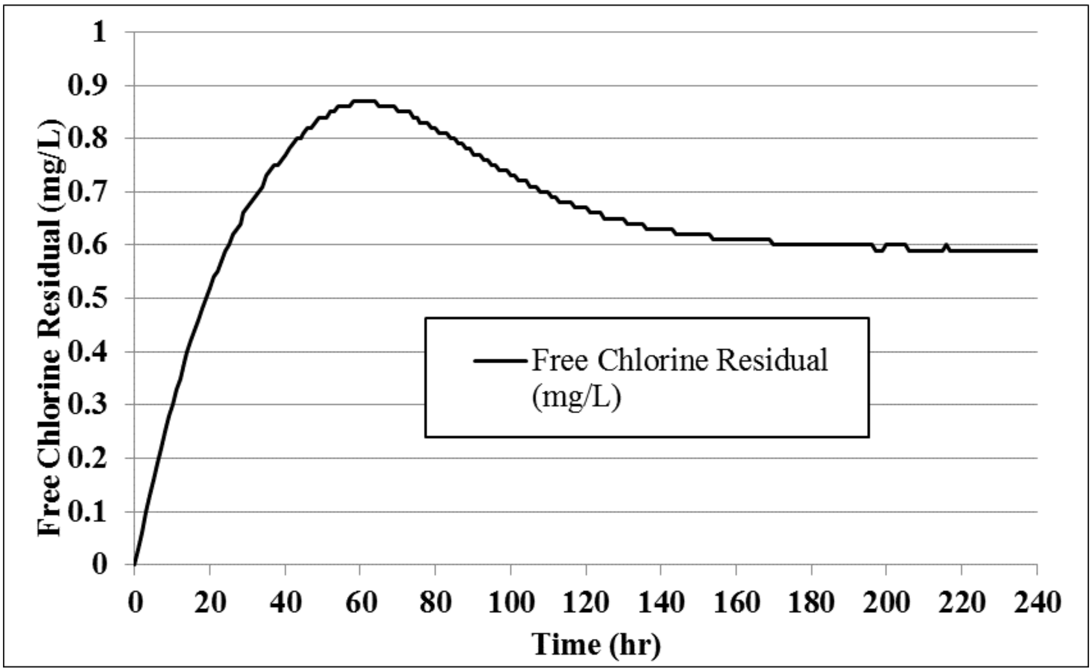


Fig.10.29. : Free chlorine residual at node DA4 (after DA Tanks)

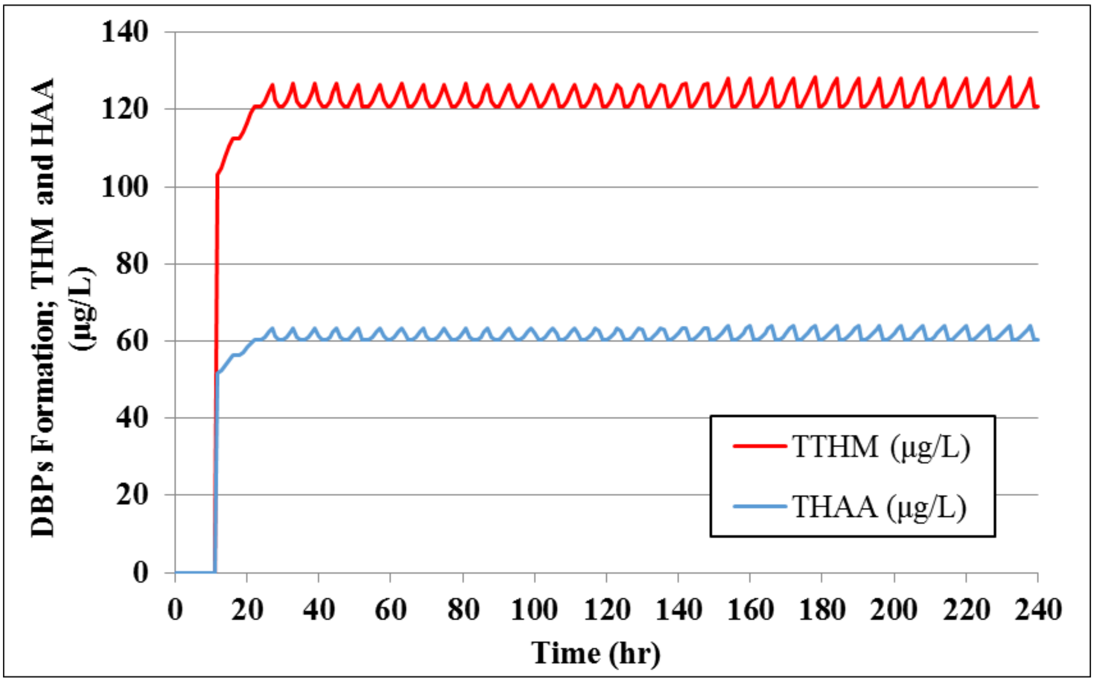


Fig.10.30. : DBPs (THM and HAA) formation at node YA1 (before YA Tank)

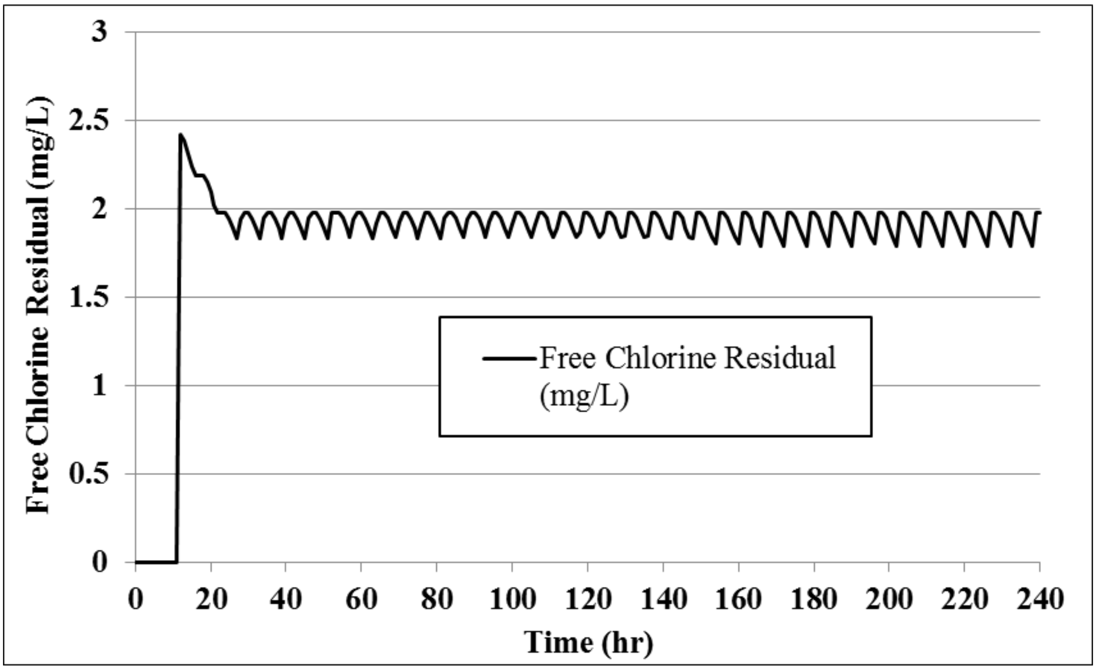


Fig.10.31. : Free chlorine residual at node YA1 (before YA Tank)

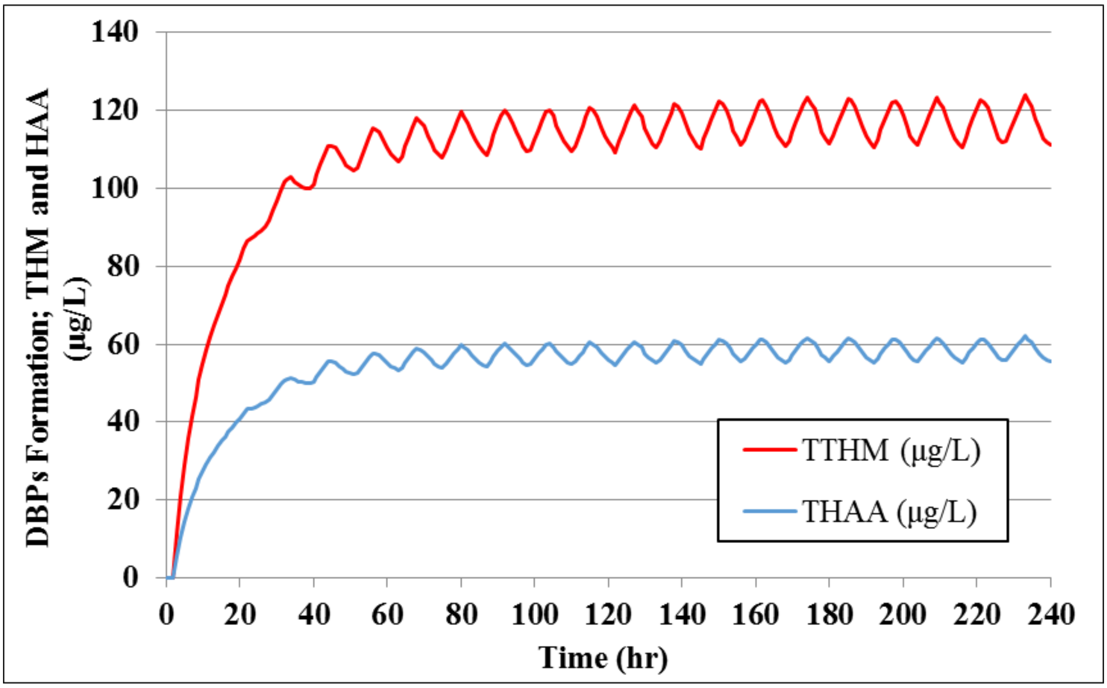


Fig.10.32. : DBPs (THM and HAA) formation at node PL3 (after PL Tank)

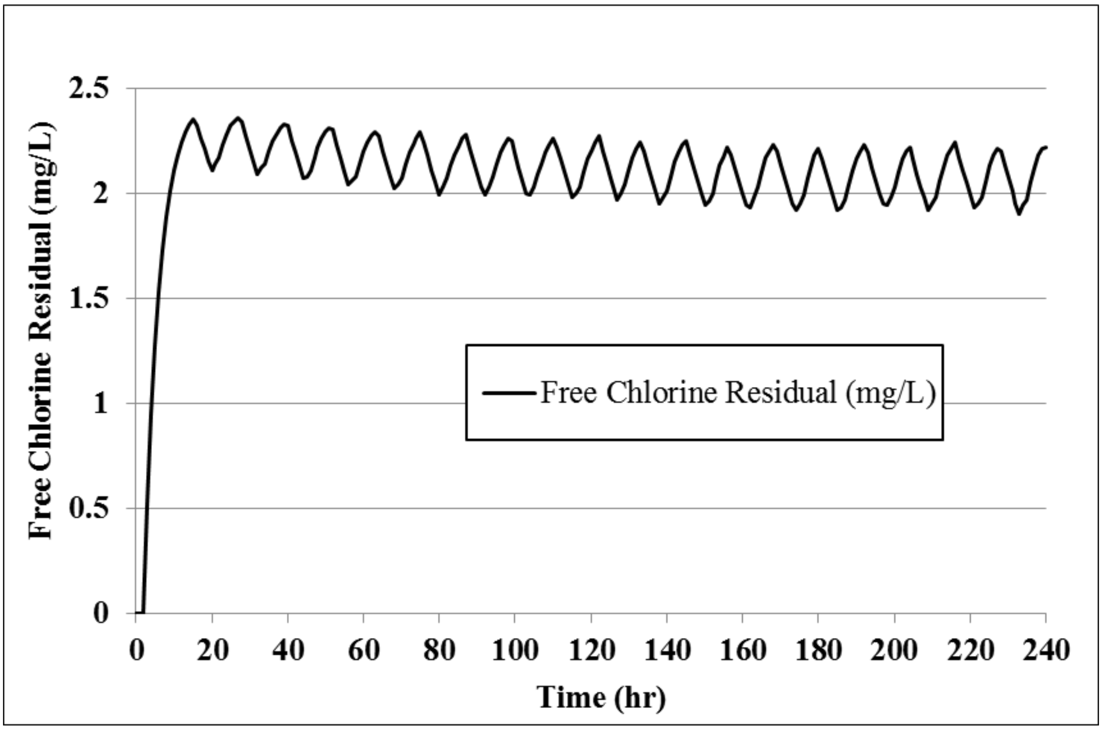


Fig.10.33. : Free chlorine residual at node PL3 (after PL Tank)

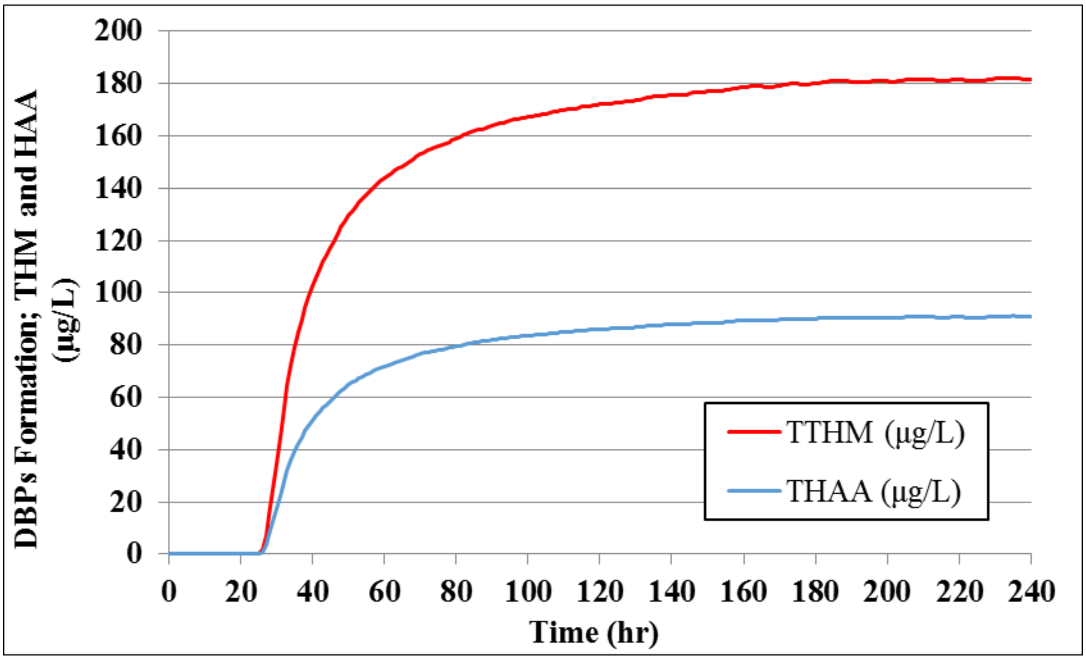


Fig.10.34. : DBPs (THM and HAA) formation at node CL3 (after CLTank)

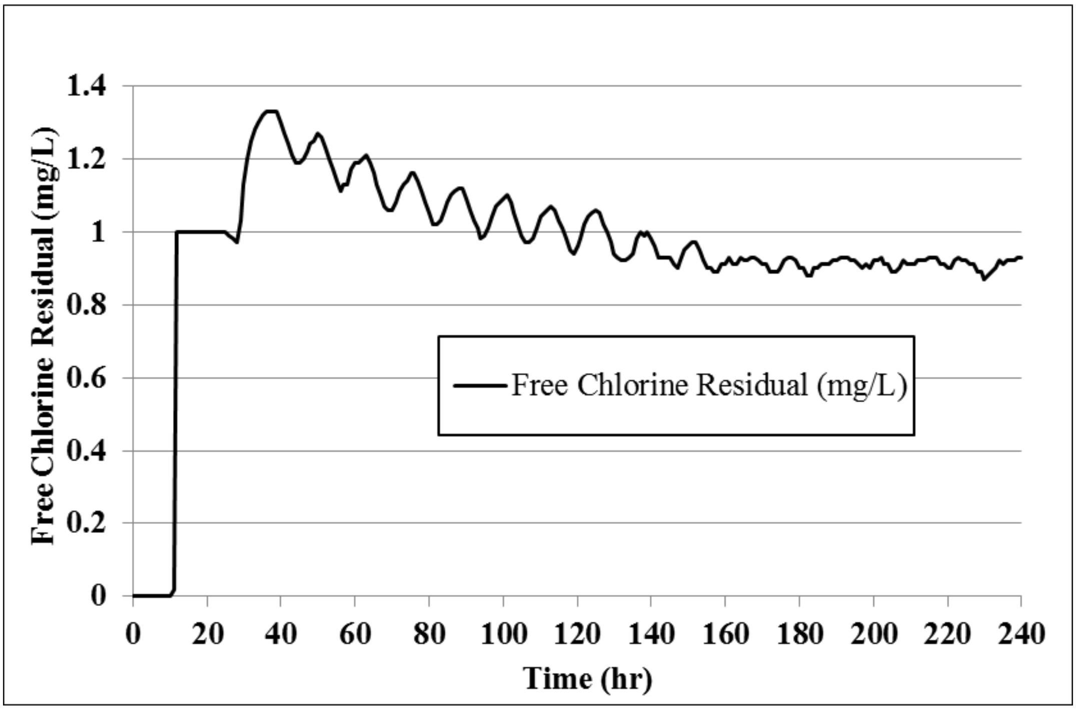


Fig.10.35. : Free chlorine residual at node CL1 (before CLTank)

Table.10.3 : Compassion of the average values obtained from on-site measurements with the predicted ones resulted from modelling process

Node	Average measured Value			Average predicted value		
	FCL (mg/L)	THMs (µg/L)	HAAs (µg/L)	FCL (mg/L)	THMs (µg/L)	HAAs (µg/L)
KA3	1	150	---	0.95	160	80
RO3	---	200	---		180^	90^
WI3	---	200	---		180^	90^
RO1	1	---	---	1.1	---	---
WI1	0.7	---	---	0.9	---	---
DA4	0.7	200		0.6	190	95
YA1	---	---	---	1.8	125	62.5
PL3	2.5	100		2.2	120	60
CL3	---	200	---	---	180	90
CL1	0.7	---	---	0.9	---	---

10.9. Conclusion

The objective of this chapter was to predict the chlorine decay and DBPs formation within a real distribution system using the parallel second order model (PSOM). For this purpose, a pilot water distribution system in Western Australia was chosen as a case study. Water samples were taken from the effluent of the Pilbara Water Treatment Plant and chlorine decay tests at the temperature of 35˚C and DBPs measurements were performed for the collected samples. Parameter estimation for the obtained chlorine decay data set was conducted using AQUASIM (numerical solution) and Excel Solver (analytical solution). Hydraulic model was generated using EPANET and water quality simulation was performed via EPANET-MSX using the results of previously performed parameter estimation. Also, measurement for on-site chlorine residuals and DBPs formation results were undertaken in key locations of the pilot water distribution system and the results were compared with the average predicted data. A very good match between the predicted results and the ones obtained from on-site measurements was found.

11. Conclusion and Recommendations for Future Research

Over years, many chlorine decay models have been proposed by several researchers. The proposed models in the literature cover a broad range of different modelling approaches; from empirical chlorine decay models to theoretical models. Empirical models are based on hypothetical relationships between chlorine concentration in water and other nominated influencing factors such initial chlorine concentration, pH of water, dissolved organic carbon (DOC), temperature, etc. with time. Theoretical models, on the other hand, define the chlorine decay as function of time using a set of dynamic process equations. These dynamic process equations are however related to physical and chemical principles such as conservation of mass between water and chemical constituents and therefore depend on kinetics of chemical reactions between chlorine and other constituents in water.

Almost all of the researchers who proposed the existing chlorine decay models in the literature claim and provide evidences that their models are amongst the most efficient chlorine decay models. However, there have been many debates and discussions between researchers and scientists about preference of some models over others. In addition, there is a growing demand amongst water utility operators and water quality auditors to seek and find more efficient chlorine decay modelling approaches which can address both planning and management applications. Therefore, an urgent need to standardize the existing chlorine decay models and propose a capable and competent method for evaluating the chlorine decay models has been recognized.

In order to provide meaningful mechanisms for evaluation of chlorine decay models, initially, the most important requirements for modelling chlorine decay need to be investigated. This step requires extensive experience in operation of water networks, water treatment facilities and water quality improvement programs. Also, having technical discussions with water utility operators and also reviewing relevant information in the literature can assist find the most prominent requirements and criteria for modelling chlorine decay in water distribution systems. This step leads to defining a general matrix of criteria for modelling chlorine decay.

The next step for providing an efficient evaluation system for managing the performance of existing and future chlorine decay models is to understand, in details, the advantages and disadvantages of the existing models when compared with the defined criteria. Access to defined performance criteria would enable the researchers and water utility authorities to improve the performance of existing models and could potentially assist propose new chlorine decay models which would generate better results. After defining the practical performance criteria for modelling chlorine decay in water distribution systems, another step is to nominate the most efficient chlorine decay models and assess their performance against the defined criteria. And finally, the best performing model shall be tested for modelling chlorine decay in an actual water distribution system.

Whilst evaluation of one nominated chlorine decay model against another model or performance assessment of the results of a chlorine decay modelling approach against one criteria (mostly accuracy of the results at one condition) has been tried by several researchers, proposing an integrated method to evaluate the performance of various chlorine decay models against a matrix of well researched criteria has not been yet undertaken. Therefore, the current research will potentially make significant contribution to the area of chlorine decay modelling within water distribution systems.

In an attempt for rectifying the defects of existing models, during the course of this research, two new chlorine decay models were proposed and evaluated against the defined criteria. This was considered as significant achievement which can add value to the novelty of the current research work.

The main objective of this research project was to develop understanding of chlorine decay and formation of disinfectant by-products using existing chlorine decay models. Following the investigation completed by a research project undertaken during previous master of philosophy study, initially, reliability of different models for different waters with various qualities was investigated, to determine the model parameters and to observe how various models fit existing measured data. Main drawbacks of the existing process-based models were discussed. Existing models with major weakness were modified to produce more reliable predictions. Then, main criteria for performance improvement of the models were defined. The nominated chlorine decay models were compared against some of the defined criteria and the best chlorine decay model was endorsed. Also, chlorine decay and formation of disinfection by-products in one of distribution systems in Western Australia was modelled as a case study. In fact, using the selected model, chlorine decay and formation of DBPs in critical points of this pilot distribution system was predicted and compared with actual measured values.

In chapter 1 of this dissertation, a brief description of the research background and the overall objectives of the research were given. Chapter 2 provided a comprehensive literature review on all aspects of chlorine decay modelling and its background.

In this chapter, existing chlorine decay models in the literature were categorized into two categories: data-based (empirical) models versus process-based (theoretical or mechanistic) models. Process-based models were given more attention due to their more popularity in the literature and their capability in predicting chlorine residuals in all planning and management applications.

Amongst all existing process-based chlorine decay models in the literature, the most popular ones including first order reaction model (FOM), second order model (SOM), parallel first order (PFOM) and parallel second order model (PSOM) were paid more attention and compared more carefully.

Chapter 3 provided information on the methodology and analytical methods for conducting laboratory experiments and performing chlorine decay analysis.

In Chapter 4, a new model was developed to improve the parallel first order model (PFOM). The new model, which was called the modified parallel first order model (MPFOM), was compared with PFOM. Similarly, In Chapter 5, new model was developed based on the extended second order model (ESOM) and was referred to as the modified second order model (MSOM). Chapter 6 discussed the most practical criteria for the selection of mathematical chlorine decay models for effective planning and management of disinfection in complex water distribution systems. Chapter 7 compared the accuracy of the results of the nominated chlorine decay models for single chlorine dosing scenarios. In Chapter 8, the models were compared for the accuracy of their results for multiple chlorine dosing scenarios. Chapter 9 compared four of the most popular models for prediction of chlorine decay in high temperatures.

Based on the information obtained from chapters 6 to 9, it is concluded that the parallel second order model (PSOM) is the most suitable process-based modelling approach for prediction of chlorine decay in water distribution system. However, there are still rooms for investigations. It is recommended that existing chlorine models be also evaluated and compared against other discussed criteria including re-chlorination scenario and also chlorine decay prediction in blended waters.

In Chapter 10, chlorine decay and formation of disinfection by-products in one of the water distribution systems in Western Australia was modelled as a case study using the selected model as the most effective model amongst all nominated chlorine decay models. It was shown that PSOM was accurately predicted the chlorine decay and formation of by-products in critical points of the nominated water distribution system.

For future research, it is recommended that the chlorine decay models discussed in this study be compared against other nominated criteria including “accurate modelling for re-chlorination scenario” and “accurate modelling of blended waters”.

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Appendices:

Appendix A1: Water Quality Characteristics and Chlorine Decay Test Dara for the Water Samples from Koechling (1998)

Table.A1.1: Water Quality Characteristics of the Water Samples from Koechling (1998)

Sample label	Description	water quality characteristics		
		DOC (mgL^{-1})	UVA_0 (cm^{-1})	Alkalinity ($mg/L\ CaCO_3$)
TRW	Trinity River, TX	4.47	0.125	95
QPW	Quittacas Pond, MA	4.55	0.165	5
CLR	City Lake Reservoir, CT	2.18	0.065	21
HRW	Hoover Reservoir, OH	3.88	0.129	92
ARW	Ashley Reservoir, MA	3.70	0.157	8

Table.A1.2: Free Chlorine Decay Test Data for Water Sample TRW (Koechling, 1998)

Time (hrs)	Chlorine Residual (mgL^{-1})	Time (hrs)	UAV (1/cm)
0.0	8.90	0.0	0.12514
0.1	7.47	0.1	0.09376
0.3	6.97	0.3	0.09010
0.5	6.67	0.5	0.08957
1.1	6.35	1.1	0.08722
2.0	6.02	2.0	0.08513
4.3	5.43	4.3	0.08120
7.4	4.93	7.4	0.07977
25.3	3.74	25.0	0.07336
48.0	2.98	48.0	0.06923
74.0	2.46	74.0	0.06635
123.0	1.74	123.0	0.06375

Table.A1.3: Free Chlorine Decay Test Data for Water Sample QPW (Koechling, 1998)

Time (hrs)	**Chlorine Residual (mgL^{-1})**	**Time (hrs)**	**UAV (1/cm)**
0.0	9.12	0.0	0.16535
0.1	7.80	0.1	0.12355
0.3	7.11	0.4	0.11762
0.5	6.63	0.5	0.11381
1.0	6.29	1.0	0.10940
2.0	5.76	2.0	0.10620
4.0	5.24	4.0	0.10144
8.0	4.57	8.0	0.09825
24.0	3.36	24.2	0.09081
48.0	2.41	48.0	0.08587
72.0	2.00	72.0	0.08237
120.0	1.17	120.0	0.07873

Table.A1.4: Free Chlorine Decay Test Data for Water Sample CLR (Koechling, 1998)

Time (hrs)	**Chlorine Residual (mgL^{-1})**	**Time (hrs)**	**UAV (1/cm)**
0.0	2.30	0.0	0.02574
0.1	2.04	0.1	0.01852
0.3	1.94	0.3	0.01670
0.6	1.81	0.6	0.01705
1.1	1.81	1.1	0.01616
2.1	1.71	2.1	0.01535
4.3	1.78	4.3	0.01720
8.0	1.53	8.1	0.01640
24.0	1.32	24.3	0.01280
48.0	1.09	48.0	0.01306
72.0	0.93	72.0	0.01333
120.0	0.77	120.0	0.01217

Table.A1.5: Free Chlorine Decay Test Data for Water Sample HRW (Koechling, 1998)

Time (hrs)	Chlorine Residual (mgL^{-1})	Time (hrs)	UAV (1/cm)
0.0	4.58	0.0	0.05995
0.1	4.42	0.1	0.04571
0.3	4.31	0.4	0.04458
0.5	4.20	0.6	0.04397
1.0	4.04	1.0	0.04348
2.0	3.95	2.1	0.04157
4.0	3.67	4.0	0.04042
8.2	3.32	8.2	0.03991
24.2	2.74	24.3	0.03622
48.0	1.91	48.0	0.03451
72.0	1.56	72.0	0.03257
120.0	1.06	120.0	0.03098

Table.A1.6: Free Chlorine Decay Test Data for Water Sample ARW (Koechling, 1998)

Time (hrs)	Chlorine Residual (mgL^{-1})	Time (hrs)	UAV (1/cm)
0.0	2.69	0.0	0.04805
0.1	2.22	0.1	0.03680
0.3	1.94	0.3	0.03434
0.5	1.89	0.5	0.03301
1.0	1.76	1.0	0.03188
2.0	1.56	2.0	0.03088
4.1	1.44	4.1	0.02976
8.0	1.27	8.0	0.02847
25.0	0.91	25.0	0.02649
49.0	0.70	49.0	0.02544
73.8	0.54	73.8	0.02435
120.0	0.35	120.0	0.02342

Appendix A2: Water Quality Characteristics and Chlorine Decay Test Dara for the Water Samples from Warton et al. (2006)

Table.A2.1: Water Quality Characteristics of the Water Samples from Warton et al. (2006)

Sample label	Description	water quality characteristics			
		DOC (mgL^{-1})	UVA_0 (cm^{-1})	pH	Alkalinity (mg/L $CaCO_3$)
A.B.W257	Warton et al. (2006)	1.8	0.058	7.97	95

Table.A2.2: Free Chlorine Decay Test Data Obtained from Warton et al. (2006)'s Study

Time (hrs)	Initial Chlorine Dosing (mg/L)			
	Cl_0=4 mg/L	Cl_0=6 mg/L	Cl_0=8 mg/L	Cl_0=10 mg/L
0	4.00	6	8	10
0.08	3.25	4.68	6.42	8.09
0.25	2.39	4.05	5.86	7.79
0.5	2.00	3.9	5.78	7.69
1	1.85	3.87	5.69	7.59
1.5	1.78	3.79	5.58	7.59
2	1.70	3.76	5.58	7.54
2.5	1.70	3.6	5.58	7.44
3	1.67	3.6	5.54	7.44
3.5	1.60	3.58	5.5	7.4
4	1.58	3.54	5.41	7.28
21	1.04	3.09	5.06	6.75
30	1.00	3.02	4.98	6.55
50	0.84	2.84	4.66	6.04
72	0.53	2.38	4.17	5.54
96	0.42	2.3	4.17	5.49
101	0.33	2.27	4.01	5.34
120	0.26	2.12	4.01	5.29
144	0.14	1.99	3.89	5.14
168	0.11	1.87	3.77	4.88

Appendix A3: Water Quality Characteristics and Chlorine Decay Test Dara for the Pilbara Post-Filtration Water (PPFW) Sample

Table.A3.1: Water Quality Characteristics for the PPFW Sample

Sample label	**Description**	**water quality characteristics**		
		DOC (mg/L)	**UV254**	**pH**
PPFW	Pilbara Post-Filtration Water	2.16	0.022	7.65

Table.A3.2: Free Chlorine Decay Test Data for PPFW Sample (25˚C)

Time (hrs)	**Initial Chlorine Concentration (Dose) (mgL^{-1})**		
	3.2	**5.4**	**8.4**
	Chlorine Residual (mgL^{-1})		
0	3.20	5.40	8.40
0.08	2.60	4.59	7.62
0.17	2.54	4.57	7.88
0.33	2.43	4.65	7.38
0.67	2.41	4.44	7.46
1	2.27	4.25	7.36
2	2.10	4.13	6.86
4	1.87	3.82	6.40
6	1.75	3.53	6.00
8	1.65	3.49	5.84
10	1.54	3.41	5.80
24	1.20	2.92	5.28
48	0.74	2.53	4.71
72	0.45	2.24	4.31
96	0.25	1.98	3.89
120	0.16	1.60	3.53
144	0.05	1.35	3.16
168	0.00	1.15	2.97
192	0.00	0.97	2.85
240	0.00	0.59	2.39

***Table.A3.3: Free Chlorine Decay Test Data for PPFW Sample (*35˚C)

Time (hrs)	Initial Chlorine Concentration (Dose) (mgL^{-1})		
	3.2	**5.4**	**8.4**
	Chlorine Residual (mgL^{-1})		
3.20	5.40	8.40	3.20
2.62	4.42	7.44	2.62
2.41	4.12	7.24	2.41
2.27	4.04	7.16	2.27
2.20	3.80	6.80	2.20
2.13	3.80	6.64	2.13
1.75	3.72	6.24	1.75
1.52	3.30	5.96	1.52
1.32	3.00	5.52	1.32
1.28	2.86	5.36	1.28
1.15	2.62	5.20	1.15
0.61	1.93	4.38	0.61
0.15	0.81	2.68	0.15
0.00	0.42	1.40	0.00
0.00	0.16	0.66	0.00
0.00	0.00	0.37	0.00
0.00	0.00	0.13	0.00
0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00

Appendix A4: Publication Abstracts

Prediction of chlorine decay behaviour using modified parallel first order model (MPFOM), a new chlorine decay modelling approach

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Abstract

Chlorine decay is usually described by the first order model (FOM) due to its easiness, although its weaknesses are well known. Second order model (SOM) was developed to compensate and address the issues of FOM. However, SOM is still incapable of accurately predicting chlorine residuals. In order to address the limitations of FOM and SOM, Parallel first order model (PFOM) was introduced and well described many chlorine decay profiles. However, PFOM suffers from a fundamental problem which is separating chlorine into two distinct parts, each part reacting independently with different substances in water. In this paper, initially, this main limitation for PFOM is explained. Then, a new model is developed based on PFOM and is referred to MPFOM. Finally, MPFOM is compared with PFOM and accuracy of its results is described in details.

Keywords

Chlrorine decay, First order model (FOM), Second order model (SOM), Parallel first order model (PFOM), Modified parallel first order model (MPFOM)

Prediction of chlorine decay behaviour using modified second order model (MSOM), a new chlorine decay modelling approach

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Abstract

One of the most well-known process based chlorine decay models is the second order model (SOM). SOM was proposed by Clark and Sivaganesan (1998) to remove the main FOM drawback, which is ignoring the impact of reactant agents. Although SOM was considered to be much superior than FOM in more accurately predicting the chlorine residuals, its prediction accuracy was still not found adequate for most of applications. The main issue of the SOM is that it substitutes all chlorine reactions with only one global reaction. As a result, SOM is unable to illustrate the initial fast and the latter slow reaction rates that have been reported in most chlorine decay tests.

In an attempt to rectify the issues of SOM, Clark and Sivaganesan (2002) extended their SOM to include both fast and slow reaction types by separating chlorine into two components, each reacting with a single organic constituent separately. In fact, Clark and Sivaganesan (2002) combined concepts of SOM and PFOM and proposed a new chlorine decay model in order to rectify the shortcomings of both SOM and PFOM. The new model contains five parameters that need to be estimated. Since their extended model had three parameters more than SOM, the model produced more accurate results for prediction of chlorine residuals. However, Clark and Sivaganesan (2002) found that the final values of the parameters of their model were very sensitive to their initial values. Therefore, it was very difficult to reach convergence during parameter estimation of their model. This issue was mentioned in Clark and Sivaganesan (2002)'s own publication. Clark and Sivaganesan (2002) had to employ a unique and complicated parameter estimation process in order to estimate the model parameters with sufficient accuracy.

In order to compare Clark and Sivaganesan (2002)'s model with other chorine decay models, the author attempted to undertake parameter estimation for their modelling approach using simple Excel Solver Add but convergence of the solution could not be obtained. However, by changing the initial values of the model parameters, in one

attempt out of ten, a solution may be found. It appears that the solution is highly dependent on the initial values of model parameters.

In this chapter, first the issue of Clark and Sivaganesan (2002)'s model is explored in more details and then a new model, called modified second order model (MSOM), will be proposed to remove the drawback of the Clark and Sivaganesan (2002)'s model. Finally, MSOM will be compared with other models and its limitations are described in more details.

Keywords

Chlrorine decay, First order model (FOM), Second order model (SOM), Modified second order model (MSOM)

Predicting chlorine decay with the parallel second order model in a water distribution system as a case study in Western Australia

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Abstract

Since the threat of Disinfection By-Products (DBP) to human health was discovered, modeling chlorine decay and its DBP formation in drinking water distribution systems is becoming very popular and challenging. Traditionally, chlorine decay is predicted according to the first order reaction scheme. However, it appeared not to be satisfactorily capable of describing chlorine decay behavior even in bulk water, which is essential for expanding the model to the real distribution system, when wall reaction is also present. Despite its complexity arising from more parameters to be estimated, the parallel second order model has been found to be more suitable for this purpose. Using AQUASIM® for parameter estimation and Multi Species Extension (MSX) module in EPANET hydraulic software, it becomes possible to implement complex and realistic water quality reaction schemes in distribution systems.

The objective of this research is to evaluate the results of chlorine decay modeling with the parallel second order approach against the actual measured data obtained from the main points in one of the Water Corporation's network. For this purpose, first, bulk water chlorine decay characteristics were examined by performing chlorine decay tests for the water samples collected from the effluent of the Water Treatment Plant where was supplying water to the network. The parameters were estimated using AQUASIM® and the hydraulic model of the distribution system was simulated in EPANET according to the existing hydraulic data. Finally, using EPANET-MSX the developed chlorine decay model was applied to the whole distribution system and the results were compared with the measured data. A very good match between the predicted results and the ones obtained from on-site measurements was found.

Keywords

Chlrorine decay, DBPs formation, parallel second order model, EPANET-MSX, AQUASIM

Comparison of the accuracy of the process-based chlorine decay models for single and multiple dosing scenarios

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Abstract:

One of the practical criteria for selection of the chlorine decay model is accurate representation of the chlorine decay behaviour. In order to compare the accuracy of different models the weighted error (sum of errors or chi^2- chi squared) between experimental and model data (χ^2) can be used as a measure of accuracy of the chlorine decay model. Error analysis performed using individual chlorine decay data set will not necessarily be adequate to represent the accuracy of a nominated model against other chlorine decay models. Hence, analysis of errors must be undertaken using adequate number of data sets and in different situations/scenarios including multiple dosing scenarios and change in water quality.

In this research work, six process-based chlorine decay models have been evaluated for the accuracy of their results for single and multiple dosing scenarios.

The nominated models are:

- First Order Model (FOM)
- Parallel First Order Model (PFOM)
- Modified Parallel First Order Model (MPFOM)
- Second Order Model (SOM)
- Modified Second Order Model (MSOM)
- Parallel Second Order Model (PSOM)

In order to compare the accuracy of the abovementioned process-based chlorine decay models, two sets of data were used. One data set was obtained from the chlorine decay test of a water sample taken from post filtration section at Pilbara Water Treatment Plant (labelled as PPFW). Another set of chlorine decay data was extracted from the research work performed by Warton et al. (2006). Data analysis for chlorine decay modelling of the selected data was performed using prepopulated Excel spreadsheets. Solver Add-in was used to undertake parameter estimation for the nominated modelling approaches. The sum of squared errors (SSE) between actual and predicted data was calculated for each data set for all models. The SSEs, which are calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy. The models were ranked based on the results of their SSE values. Lower the SSE of the model was, the higher the model was ranked. MSOM and PSOM were ranked first and second amongst all nominated models. Although MSOM was ranked better than PSOM with regards to accuracy of the predicted chlorine residuals, it should be noted that MSOM contained five parameters compared to only four parameters of the PSOM and thus MSOM produced more accurate results than PSOM due to having more model parameters. Also, it was noticed that the difference in accuracy of the results between MSOM and PSOM was negligible. Therefore, it was concluded that the PSOM was the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water for single and multiple dosing scenarios.

Keywords

Chlorine decay, First Order Model (FOM), Parallel First Order Model (PFOM), Modified Parallel First Order Model (MPFOM), Second Order Model (SOM), Modified Second Order Model (MSOM), Parallel Second Order Model (PSOM)

Evaluation of Process-Based Chlorine Decay Models against Temperature Variation for Multiple Dosing Scenario

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Abstract:

In this research, six process-based chlorine decay models were evaluated for the accuracy of their results considering simultaneous effects of multiple chlorine dosing and temperature variation. The nominated models are:

- First Order Model (FOM)
- Parallel First Order Model (PFOM)
- Modified Parallel First Order Model (MPFOM)
- Second Order Model (SOM)
- Modified Second Order Model (MSOM)
- Parallel Second Order Model (PSOM)

In order to compare the accuracy of the abovementioned process-based chlorine decay models, two different sets of chlorine decay data were used for the accuracy assessment of the six nominated process-based chlorine decay models. The two sets of data were acquired by undertaking chlorine decay tests on water sample taken from Harding Dam Water Treatment Plant at temperatures of 25°C and 35°C.

Data analysis for chlorine decay modelling of the selected data has been performed using prepopulated Excel spreadsheets. Solver Add-in is used to undertake parameter estimation for the nominated modelling approaches. For each model, parameters were defined based on the analytical solution/formula of the model. An initial value was assigned for each model parameter. An extra parameter of E/R was also defined for each model to account for temperature effect. Reaction rates for the nominated temperatures were then calculated based on Arrhenius equation.

Data analysis could not be completed for MPFOM and MSOM due to occurrence of calculation error while parameter estimation was being undertaken by Solver Add-in. It was identified that the reason for errors was due to high number of model parameters and also limitation of Excel Spreadsheets for performing calculations of big numbers. As a result, evaluation of temperature variation was not completed for these two models and was only undertaken for FOM, SOM, PFOM and PSOM. For all these models, the chlorine residuals have been predicted for each data set over the entire retention time with maximum one hour intervals. The sum of squared errors (SSE) between actual and predicted data was calculated for each data set for all models. The SSEs, which were calculated for each data set, have then been compared for all nominated models to evaluate the models accuracy. R squared values were also calculated and compared for each set of data for all nominated models.

The models were ranked based on the results of their SSE values. Lower the SSE of the model was, the higher the model was ranked. PSOM were ranked first. Therefore, it is concluded that the PSOM is the most accurate process-based chlorine decay models for modelling chlorine decay in bulk water with effect of multiple chlorine dosing and temperature variation.

Keywords

Chlorine decay, First Order Model (FOM), Parallel First Order Model (PFOM), Modified Parallel First Order Model (MPFOM), Second Order Model (SOM), Modified Second Order Model (MSOM), Parallel Second Order Model (PSOM)

Effect of known dissolved organic nitrogen addition on chlorine decay profile of a surface water and its implications

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Abstract:

Chlorine dosed for disinfection purposes decays due to reactions with natural organic matters - both carbonaceous and nitrogenous organic compounds, and inorganic compounds. Like Dissolved Organic Carbon (DOC) as an indicator of Natural Organic Matter (NOM) in surface water, Dissolved Organic Nitrogen (DON) such as ammines would have also a relatively significant influence on chlorine decay and therefore on the formation of Disinfectant By-Products (DBPs). It has been recently shown that the formation of DBPs in bulk water is affected by the amount of DON and the impact is truly different from the effect of DOC. Reaction with DON can result in combined chlorine in the form of organochloramines. These compounds are traditionally neglected, but the finding of NDMA as a carcinogenic disinfectant by-product requires consideration of combined chlorine, if NDMA formation in chlorinated waters is to be modeled. Fisher et al., (1996) provided the necessary scheme to consider combined chlorine in waters, and showed the scheme could be useful in describing major chlorine species (combined chlorine and free chlorine) in surface waters. However, the real of impact of addition of dissolved organic nitrogen, known to form disinfection by-products such as NDMA is not fully understood. This paper attempts to fill such gap by adding known organic nitrogen compound, especially aspartic acid, into the water and by observing its decay characteristics and by estimating parameters necessary to define the model using Aquasim®. Results showed that the scheme provided by Fisher et al., (1996) is useful in describing such relationship.

Keywords

Chlrorine decay, DBPs formation, parallel second order model, DOC, NDMA, AQUASIM

Practical criteria for modelling chlorine decay in water distribution systems-A critical review

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Abstract:

There are two main objectives/goals that have been defined for disinfection of drinking water supplies. The first objective is mainly to remove harmful microorganisms in drinking water before it reaches any consumers (primary disinfection). The second objective is to maintain a minimum concentration of the disinfecting agent throughout the distribution system to prevent microbial growth and to reduce the effect of potential contamination (secondary disinfection).

Chlorine is believed to be the best candidate amongst all disinfectant agents in achieving both of abovementioned objectives for disinfection of drinking water supplies. Due to its low cost, high efficiency in deactivating bacteria, ease of application and monitoring, till now chlorine is believed to be the most commonly used disinfectant (Hua et al., 1999). However, as a chemical agent, chlorine reacts with many substances and particles in water and on the pipe wall and, as a result, its concentration decreases as it travels through the distribution system. This is known as chlorine decay. As chlorine decays, it loses its potential to effectively achieve the main objectives of disinfection of water in distribution systems (primary and secondary disinfection). In order to overcome this issue more chlorine can be added to water to compensate its decay. However, the amount of chlorine added to the water is very important. If the initial chlorine dosing concentration is too low, there may not be a residual left at the end of the distribution system to protect against reoccurrence of any potential contamination. If the dosing rate is too high, it can lead to customer complaints, corrosion of the pipe network or the formation of by-products, including trihalomethanes (THMs), which are suspected carcinogens.

It has been adequately emphasized and understood that modelling of chlorine decay is required in order to effectively estimate and manage the chlorine residual and its by-products within existing water networks (management application) and also for new systems (planning application). As discussed earlier, there are some requirements that have to be met in order for a chlorine decay model to efficiently estimate the chlorine residual within a distribution system and assist in achieving the planning and management goals of the chlorination.

There are many chlorine bulk decay models within the literature, some of which have been discussed previously. Each model has particular characteristics, capabilities and also weaknesses with regards to meeting the requirements and successfully pursuing the objectives of modelling chlorine decay. Therefore, in order to select the best modelling approach for chlorine decay modelling of a water supply network of interest, firstly, these requirements have to be clearly understood.

In this paper, basic requirements (criteria) for effective chlorination and chlorine decay models are explained and finally the most popular existing chlorine decay models were characterized. Existing chlorine decay models in the literature were categorized into two categories: data-based (empirical) models versus process-based (theoretical or mechanistic) models. Process-based models were given more attention due to popularity in the literature and their capability in predicting chlorine residuals in all planning and management applications. Amongst all existing process-based chlorine decay models in the literature, the most popular ones including first order reaction model (FOM), second order model (SOM), parallel first order (PFOM) and parallel second order model (PSOM) are investigated in more details and their performance is evaluated against defined criteria.

Keywords

Chlrorine decay, DBPs formation, parallel second order model, DOC, NDMA, AQUASIM