THE MANAGEMENT OF TRIHALOMETHANES IN WATER SUPPLY SYSTEMS

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Abstract

The formation of potentially harmful trihalomethanes (THM) when using chlorine as a disinfectant in potable water supplies has led to tighter regulatory controls and hence a need for better models for THM management. The prediction of THM concentration is difficult due to the complex and changing hydrodynamic and chemical regimes found in water treatment works (WTWs) and distribution systems.

The purpose of the study is to increase understanding of THM formation and chlorine decay through six water treatment works (WTWs) and distribution systems operated by Severn Trent Water Ltd and ultimately develop an efficient, robust, cost effective model for chlorine decay and THM formation.

With knowledge of the bulk chlorine decay characteristics and the THM productivity of the water, this model offers a simple and straightforward tool which can be readily applied to WTWs and distribution systems alike to provide an initial assessment of the risks of total THM formation at different sites, and to identify sites and systems at risk of compliance failure. Relying only on the measurement of analytically undemanding parameters (in particular, chlorine and its decay with time), under appropriate circumstances this model offers advantages of simplicity and cost-effectiveness over other, more complex models. The model can thus be applied to assess the chemical risk under different scenarios allowing for informed decision making.

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Abbreviations

AOC	Assimilable organic carbon
ARE	Average Relative Error
AWWARF	American Water Works Association Research Foundation
BIF	Bromine incorporation factor
Br	Bromide concentration (µg/l)
BPS	Booster pumping station
$CHBr_2Cl$	Chlorodibromomethane (µg/l)
$CHBrCl_2$	Bromodichloromethane (µg/l)
$CHBr_3$	Bromoform (µg/l)
$CHCl_3$	Chloroform (µg/l)
Cl	Free chlorine concentration (mg/l)
C_0	Initial free chlorine concentration (mg/l) at time, t (hours)
CSO	Combined sewage overflows
CSTR	Continuous stirred tank reactor
DAF	Dissolved Air Floatation

DBP	Disinfection by-product
DOC	Dissolved Organic Carbon
DPD	Diethyl-p-phenylendiamine
DSR	Distribution service reservoir
EBCT	Empty bed contact time
EU	European Union
FEH	Flood Estimation Handbook (Centre for Ecology and Hydrology, UK)
F.T.U	Formazin turbidity unit
GAC	Granular activated carbon
HAA	Haloacetic acid
HBC	Hopper Bottom Clarifier
HOBr	Hypobromous acid
HOCl	Hypochlorous acid
IARC	International Agency for Research on Cancer
K_B	Bulk chorine decay constant (l/hr)
K_W	Wall chlorine decay constant
km	Kilometres
MCL	Maximum contaminant level
mg/l	Milligrams per litre
Ml/d	Mega-litres per day
NCI	National Cancer Institute
N.T.U	Nephelometric turbidity unit
NOM	Natural organic matter
OBr^-	Hypobromite ion

OCl^-	Hypochlorite ion
PAC	Powdered activated carbon
PHL	Public Health Laboratories (University of Birmingham)
R^2	Correlation coefficient
RGF	Rapid gravity filter
RMS	Root mean squared error
s.d.	Standard deviation
SPSS	Statistical Package for Social Sciences
STL	Severn Trent Laboratories
STW	Severn Trent water
SUVA	Specfic ultraviolet absorbance
THM	Trihalomethane (µg/l)
THMFP	Trihalomethane formation potential (µg/l)
TTHM	Total trihalomethane (µg/l)
TOC	Total organic carbon (mg/l)
TOX	Total organic haloform
UK	United Kingdom
UoB	University of Birmingham
USEPA	United States Environmental Protection Agency
UV_{254}	Ultraviolet light absorbance at 254 nanometres
WHO	World Health Organisation
WRc	Water Research Council
WTW	Water treatment work
µg/l	Nanograms per litre

Chapter 1 Introduction

1.1 General

The famous artist, scientist and theorist, Leonardo Da Vinci, once said:

"*Water is the driver of nature*"

Half a millennium later this view still remains pertinent to people around the world, since without water, life cannot exist.

Historically, communities developed around water sources, often at convenient crossing points on rivers, where a source of drinking water and route of waste disposal was readily available. For centuries, 'good water' was defined as water that was clear, pleasant to the taste and not malodorous. It was not until the discovery that water could be a major vehicle of disease in the middle of the 19th century (preceding the scientific verification of the germ theory of disease later in the same century) that attitudes towards drinking water began to change.

A major objective of drinking water treatment since then has been to provide water that is both microbiologically and chemically safe for human consumption. The combination of drinking water treatment along with disinfection has proven to be one of the major public health advances in modern times (Clark & Sivaganesan, 2002). Indeed, Life magazine, in rating the 100 most important historical events and people of the previous millennium, called drinking water chlorination and filtration "*…probably the most significant public health advance of the millennium*", ranking it 46th in its list (Life Magazine, 1998).

Following the use of continuous application of chemical disinfectants, starting in the early 1900s in Europe and the USA, outbreaks of diseases attributable to waterborne pathogens, such as typhoid and cholera, dramatically declined in developed countries. Chlorine became the most widely adopted and revered disinfectant for water treatment worldwide, because of its potency, relative ease of use, lasting residual, and cost effectiveness (Freese *et al.*, 2004).

Its reputation as the 'disinfectant of choice' remained untarnished until 1974, when evidence published separately by Rook (1974) and Bellar *et al.* (1974) showed chloroform in drinking water resulted from the reaction between chlorine and natural organic matter. Since that time, extensive research has shown a variety of halogenated disinfection by-products to be formed through the use of chlorine, including trihalomethanes (THMs), haloacetic acids, haloaldehydes, haloketones, haloacetonitriles, chloropicrin and chlorophenols (Nikolaou *et al.*, 1999; Richardson *et al.*, 2007). Of the more than 300 disinfection by-products that have been reported from the use of chlorine disinfection, THMs have received the most attention (both scientifically and regulatory) due to their widespread occurrence and the reported health concerns.

The discovery of chlorinated disinfection by-products in drinking water led to a change in the attitude towards chlorination and a rethinking of the general management of potable water supply systems. As a response to public perception and tightening legislation, approaches to controlling DBP formation have included applying alternative disinfectants and/or reducing the quantity of chlorine applied. Recent large outbreaks of waterborne illness, however, such as cholera in Peru during the early 1990s, cryptosporidiosis in Milwaukee, USA in 1993, and E. coli induced gastroenteritis in Walkerton, Ontario, Canada in 2000, have served as dramatic reminders of the need for proper disinfection control of waterborne pathogens in drinking water.

The driving force, therefore, of modern water treatment, is obtaining an optimum balance between bacteriological safety, the formation of DBPs, and providing customers with water that they find pleasant to drink at a cost-effective price. In order to achieve this, it is necessary to understand and predict both the formation of DBPs and the decay of chlorine, in relation to source water, treatment processes, storage and supply.

1.2 Study objectives

The purpose of this study was to improve the management of THM through developing a better knowledge of chlorine decay and THM formation through six water treatment works (WTWs) and distribution systems operated by Severn Trent Water (STW). Ultimately, the study aimed to develop efficient, robust, cost effective models for chlorine decay and THM formation, which can be used in the operational management of potable water treatment works and distribution systems. The specific objectives were:

i. To undertake a detailed analysis and cross comparison of THM formation and chlorine decay in six water supply systems, relating the differences to WTW operational and source water characteristics, supply procedures, and temporal and spatial variation in each of the foregoing, in order to try and understand critical factors in each of the six systems.

ii. To investigate the influence of water quality parameters, initial chlorine concentration, temperature, contact time, water treatment unit and supply processes on chlorine decay, in order to develop empirically based models to relate functional dependencies to each other.

iii. To investigate THM formation in relation to key water quality parameters, initial chlorine concentration, temperature, contact time and water treatment unit and supply processes, and consequently to determine appropriate THM formation models.

iv. To consolidate the analysis into a cost-effective, spreadsheet model that can be practically applied in operational circumstances, enabling the user to enter prevailing water quality and WTW operational characteristics to predict chlorine use and THM formation from source water to customer tap.

v. To apply and critically evaluate the proposed model for one of the supply systems studied, thus identifying mitigation strategies for the management of THMs.

1.3 Project organisation

The project builds on research undertaken previously at the University of Birmingham (UoB) for STW in this topic area. A good working relationship has existed throughout the project with a number of STW personnel, particularly with the collection of data at WTWs and distribution systems.

The study was organised into four major areas; 1. investigational field work and sampling programs at WTWs and distribution systems; 2. conjunctive laboratory bench-scale studies at UoB laboratories; 3. data analysis; 4. modelling work and application to operational scenarios.

The author has planned, collected and performed the majority of experimental work in collaboration with UoB staff. Severn Trent Laboratories (STL) carried out analysis of all TOC, THM, and bromide samples taken during the study. Data from STW databases were also utilised. The author carried out all subsequent analysis.

The commercial nature of the study has meant that whilst the study aims to fulfil the objectives of the author, it was also aiming to directly link with the needs of STW. Objectives were therefore largely based around the perceived needs of STW. This reflects the nature of the topic studied and a desire to meet the needs of industry for research that can be directly applied at operational, design and research levels, whilst also meeting the requirements of the degree of PhD.

1.4 Structure of thesis

The subsequent chapters of the thesis are structured in the following way:

Chapter 2 – Literature review: An introduction to the physical, chemical and biological processes of relevance to the study is provided. A critical review of the existing published work on water quality in water treatment works and distribution systems, with specific emphasis on THM formation and chlorine decay is presented. The knowledge gap is defined and justification is given for the objectives of the study.

Chapter 3 – Materials and methods: Terminology and details of the experimental procedures used in this study both at the UoB and in the field work are described. Details are also given to the methodology for tests at STL. A brief summary of the study sites is then provided.

Chapter 4 – System response: The results and analysis of data on water quality, collected throughout the WTWs and distribution systems during the study are presented in conjunction with data from STW databases. The response of the six water supply systems to changes in water quality, seasonal effects and treatment practices are discussed and analysed.

Chapter 5 – Chlorine decay: The results, analysis and conclusions of a substantial number chlorine decay experiments conducted under both ambient and laboratory conditions are described. An investigation into the significance of the main parameters influencing bulk chlorine decay is made with specific emphasis placed on contact tank operations. Predictive equations are presented and their accuracy quantified.

Chapter 6 – THM formation: The formation of THM at the WTWs and distribution systems is considered. Results of a number of experiments to determine THM formation on a temporal scale in relation to key parameters are presented and semi-empirical formulae for predicting THM formation are developed.

Chapter 7 – Modelling and management options: Compiling the results, analysis and knowledge gained from previous chapters, a spreadsheet-based model is created to represent one of the six WTWs. The workings, limitations and accuracy of results from the model are presented. The model is used to investigate the potential changes in water quality and treatment practices, and its applicability to the other WTWs explored. The management implications of these changes are also discussed.

Chapter 8 – Conclusions and future work: The conclusions from this study are drawn together and recommendations for future research are made.

1.5 Publications

Brown, D., West, J.R., Courtis, B.J. and Bridgeman, J., "Modelling THMs in Water Treatment and Distribution Systems", accepted by *ICE Proceedings – Water Management*.

Chapter 2 Literature Review

2.1 Disinfection by-products and the shift in disinfection practice

Disinfection in potable water treatment may be defined as the reduction of pathogenic organisms to prevent waterborne diseases (Haas, 1999). Many techniques of disinfection are practised, some more common than others, including the use of chlorine, potassium permanganate, ultraviolet light and ozone. In the United Kingdom, chlorine is undoubtedly the most commonly applied disinfecting agent on the grounds of a number of advantages. Primarily, it is a very effective disinfectant, it is relatively easy to handle, the capital costs of installation are low, it is cost effective, simple to dose, measure and control, and it has a relatively prolonged residual (Freese *et al*, 2004; Sadiq & Rodriguez, 2004; Warton *et al*., 2006).

The role of chlorine as the ‘disinfectant of choice’ remained unchallenged until 1974, when independent research by Rook (1974) and Bellar *et al*. (1974) determined the presence of chloroform in chlorinated drinking water. Since then DBPs have been actively investigated, with significant research effort being directed towards increasing our understanding of DBP formation, occurrence and health effects.

A large number of epidemiological studies have repeatedly shown an association between the consumption of chlorinated drinking water, or exposure to it, and bladder, colon and rectal cancers in laboratory animals (IARC, 1991; Morris *et al.*, 1992; Cantor, 1994; WHO, 2005). Additionally, toxicology studies have shown THMs and other DBPs to be carcinogenic or to cause adverse reproductive or developmental effects in laboratory animals (Nieuwenhuijsen *et al.*, 2000; Graves *et al.*, 2001; Villanueva *et al.*, 2007). While each of these studies have tended to be inconclusive with regard to their findings concerning the health effects of human consumption of chlorinated drinking water, the sheer weight of evidence provided by these studies is cause for concern (Singer, 1999).

As a result, a 'precautionary principle' has been adopted by many national and international agencies to regulate THMs and other DBPs in drinking water primarily through maximum contaminant levels (MCLs). With more stringent standards likely to be implemented in the future as knowledge and analytical techniques improve, the water industry is being forced to gain a better understanding of the effectiveness and risks of disinfection.

2.2 History of chlorination

One of the first documented uses of chlorine was in 1854 when, following an outbreak of cholera, John Snow attempted to disinfect the water supply around the locality of the affected Broad Street pump in London (White, 1986). Continuous chlorination of potable water supplies began around the beginning of the twentieth century, and resulted in a dramatic reduction in deaths due to typhoid, cholera and other water-borne diseases (Baxter, 1995). This practice, termed simple or marginal chlorination, predominantly consisted of adding chlorine or chlorine affiliates to water, commonly after filtration. Since that time the endorsement and prevalent application of free residual chlorine evolved as a result of developments in our knowledge of chlorination chemistry and the biocidal capabilities of various forms of chlorine (Akin *et al.*, 1982; USEPA, 1999).

2.3 Basic chlorine chemistry

The basic chemistry of chlorine in relation to potable water supply has been studied by a large number of workers (for example, Fair & Geyer, 1954; Faust & Aly, 1983; White, 1986; AWWARF, 1996; Powell, 1998; Haas, 1999). This section summarizes the main features.

Chlorine is typically applied in water treatment in the form of compressed gas under pressure (that is dissolved in water at the point of application), solutions of sodium hypochlorite, or solid calcium hypochlorite. Essentially, the three forms are chemically equivalent because of the rapid equilibrium that exists between dissolved molecular gas and the dissociation products of hypochlorite compounds (Haas, 1999). The following equations depict the reactions of the three compounds in pure water:

Gaseous chlorine: $Cl_2 + H_2O \leftrightarrow H^+ + Cl^- + HOCl$ (2.1)
Sodium hypochlorite: $NaOCl + H_2O \leftrightarrow H_2O + Na^+ + OCl^-$ (2.2)
Calcium hypochlorite: $Ca(OCl)_2 + 2H_2O \leftrightarrow Ca^+ + 2OH^- + 2HOCl$ (2.3)

Of importance, the use of chlorine gas will depress the pH of the water, whereas dosing with hypochlorite solutions increases the pH (AWWARF, 1996). The total concentration of molecular chlorine, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) is defined as 'free available chlorine'. Combined chlorine represents the amount of chlorine that is in chemical association with various other compounds (usually ammonia, nitrogen or other organic compounds) and total chlorine is the sum of both free and combined chlorine. Whilst combined chlorine has a disinfecting power it is usually by no means as efficient disinfectant as free chlorine (White, 1986; Haas, 1999).

HOCl will dissociate to give hydrogen ions (H^+) and hypochlorite ions:

$$HOCl \leftrightarrow H^+ + OCl^- \tag{2.4}$$

The dissociation of the HOCl is reversible and dependant on both pH and temperature (Figure 2.1). High pH values drive the equation (2.4) to the right (*i.e.* favouring the formation of the hypochlorite ion), whilst lower pH values drive the equation to the left, with a predominance of hypochlorous acid. For example:

At 20°C:	pH 5	99.7% will be HOCL
	pH 8	23.2% will be HOCL

Maintaining a predominance of HOCl is important due to the fact that pathogen surfaces naturally carry a negative electrical charge. These surfaces are therefore more readily penetrated by the uncharged, electrically neutral HOCl than the negatively charged OCl^-. HOCl is approximately eighty times more powerful as a disinfectant than OCl^- (White, 1974). Due to the pH dependency, it is common practice that disinfection with chlorine is conducted at pH values of less than 9, with the STW standard being approximately 8 (STW Design Manual, 2006).

Some argument still exists with respect to the actual killing mechanism of bacteria using chlorine, although it is generally agreed that the relative efficiency of various disinfectants is a function of the rate of diffusion of the active agent through the bacteria cell wall. It is assumed that the disinfecting agent has the ability to attack enzymes within the cell and their destruction results in the death of the cell. The other major factors other than pH that influence the efficiency of chlorine disinfection are:

- Temperature;
- Type and concentration of the organisms to be killed;
- Concentration of chlorine;
- Nature of the water undergoing treatment;
- The water’s exposure to chlorine (*e.g.* by ‘particle sheltering’ of organisms in water);
- Maintenance of a suitable concentration for a defined period (commonly assessed by the *Ct* concept, where *C* refers to the final concentration of free chlorine (mg/l) and *t* refers to the contact time (minutes) required to in-activate a specified percentage of micro-organisms).

2.4 Chlorine decay mechanisms

Chlorine is a non-selective oxidant, and therefore reacts with both organic and inorganic substances in the water as well as functioning as an antimicrobial agent. Generally, in natural waters, the species that are most reactive with chlorine are inorganic substances in a reduced valence state such as iron, manganese, sulphide, bromide and ammonia (Wei *et al*., 1974; Vasconcelos *et al.*, 1997; Warton *et al*., 2006; Jegatheesan *et al*., 2008; Deborde & von Gunten, 2008). These reactions are relatively quick, occurring within seconds to hours. Chlorine will also react with organic substances in the water, although these reactions usually proceed at a slower rate dependant on the nature of the species present. As both organic and inorganic particles are present in varying concentrations and have different degrees of reactivity, the loss of chlorine over time is a gradual process. The half-life of chlorine in treated water (*i.e.* the time it takes for 50% of the initial chlorine to dissapear) can vary from several hours to several days (Clark & Sivaganesan, 2002).

Being a strong oxidizing agent, in distribution systems, chlorine may also react with the material in the pipe walls, as well as the attached biofilm and miscellaneous accumulated sediment. The consumption of chlorine within the bulk aqueous phase is often referred to as the bulk decay, while that due to biofilms and at the distribution pipe wall are known as the wall decay (Biswas and Clark, 1993; Clark *et al.*, 1994a; Beatty *et al.*, 1996; Vasconcelos *et al*., 1997; Powell, 1998). The sum of the two processes is commonly termed the ‘chlorine demand’ of a given water (Warton *et al*., 2006).

2.5 Bulk chlorine decay

Since knowledge of the consumption of chlorine due to reactions with individual organic and inorganic chemicals in the aqueous phase is limited, modelling of reaction kinetics has been based on the consideration of the following global reaction:

$$\text{Cl} + \text{Reac} \rightarrow \text{Products} \tag{2.5}$$

Where ‘Cl’ is the chlorine (or chlorine affiliates) concentration and ‘Reac’ refers to the species that can potentially react with it. Due to the complexity and the fact that the exact composition of ‘Reac’ remains unknown, chlorine decay models developed have adopted a ‘black box’ approach, where reactions are not considered separately, but rather as a whole with global velocity and kinetics representing the fate of the disinfectant (Vieira *et al*., 2004; Jegatheesan *et al*., 2008).

In one of the earliest attempts to model chlorine decay, Feben & Taras (1951) investigated (total) chlorine decay over 24-hours in raw river water dosed with up to 1.5 % volume of raw sewage. The rate of decay was found to be exponential; increasing with both temperature and sewage content, although it was observed that there was a rapid initial decay, attributed to the ammoniacal (break-point) reactions. They proposed the following equation:

$$C_t = C_1 t^n \tag{2.6}$$

Where: C_t = Chlorine consumed at time, t (hours),

C_1 = Chlorine consumed after 1-hour

n = Constant (determined experimentally).

Haas and Karra (1984) investigated several models to describe chlorine decay, including (as defined in Vieira *et al.*, 2004);

- *First-order decay (with respect to chlorine)* - where the reaction velocity is proportional to the concentration of the reactant, the constant of proportionality being the decay constant (K).
- *Power-law decay (nth order)* – where the reaction velocity is proportional to the n^{th} power of chlorine concentration.
- *Limited first-order decay* – where it is assumed that a fraction of the initial chlorine concentration, C^*, remains unchanged and only the remainder, C_0- C^*, decays exponentially according to a first order law.
- *Parallel first-order decay* – assumes two components to the reaction, each decaying according to a first order law, but with different decay rate constants (K_1 and K_2).
- *Second order decay* – with respect to chlorine and all other reactants that contribute to its consumption. Assumes that the velocity of the reaction is proportional to the concentrations of both species.
- *Zero order* – where the reaction rate is independent of the concentration of the reactant.

They found the parallel first-order decay model yielded the most accurate results, due to the presence of slow and fast reacting components in the water. However, the applicability of the results to potable water is dubious, as they used sewage effluent in their study and used initial chlorine dosages of up to 10 mg/l.

A number of models make use of a sequence of different models (either first- or second-order, or with different kinetic parameters). Qualls & Johnson (1983) described the short-term chlorine consumption by fulvic acid in experiments over five-minutes. They described chlorine decay as the sum of two first-order equations; the first describing the rapid reactions occurring in the initial 30 seconds, and another slower process continuing throughout the remainder of the experiment. They found the amount of chlorine consumed in the initial fast process varied relatively little among different chlorine concentrations for a particular carbon concentration except for cases where the amount of chlorine added was low and almost exhausted in the initial period. Chlorine decay in the second stage was nearly linear and approximately parallel for different initial concentrations.

A substantial amount of chlorine decay work was conducted on water sampled at the Choisy-le-Roi water treatment plant near Paris in the early 1990s. Ventresque *et al*. (1990) carried out a series of tests to analyze the bulk decay kinetics in relation to organics of water sampled through the treatment plant, which consisted of pre-ozonation, clarification, sand filtration, ozonation, GAC, bio-adsorption and post-chlorination. They found that the initial chlorine demand and the kinetic constants of ozone / GAC treated water were always lower than those obtained from sand filtered water. Jadas-Hécart *et al*. (1992) also attempted to identify the organic compounds that react with chlorine in the final water leaving the same treatment plant. As with Qualls & Johnsons' (1983) work, they divided chlorine decay into two phases. The first 4-hour period was termed the 'initial chlorine demand', characterised by fast reactions with chlorine. The second, slower consumption phase after the first 4-hours was defined as the 'long-term demand', which was interpreted with the following kinetic equation:

$$-dx/dt = k_b' (A - x)^a (B - \{x/s\})^ß \qquad (2.7)$$

Where:

x = Chlorine consumed at time t

k_b' = Rate constant (2nd order)

A = Total chlorine residual at 4-hours

B = Concentration of reactants at time, t = 4-hours

a = Partial order with respect to chlorine

$ß$ = Partial order with respect to reactants

s = Stoichiometry

The values of a, ß and s were assumed to equal unity, producing a second order reaction with respect to chlorine and one other reactant:

$$-dx/dt = k_b' (A - x) (B - x) \qquad (2.8)$$

Zhang *et al*. (1992) studied the modelling of chlorine decay in sand filtered water (prior to contact tank chlorination, but after pre-chlorination) at the Macao water treatment plant in south China. Again, the study indicated that chlorine decay could be split into two phases; an initial consumption during the first hour (representing the time spent in the contact tank and the remainder of the WTW), and a long-term chlorine consumption after 1-hour in the distribution system. A first order model was found to describe the second phase accurately.

Clark & Sivaganesan (2002) used second-order models for both time intervals, and instead used t = 1-hour as the boundary between the separate periods. The USEPA Water Treatment Plant model (USEPA, 1992) described chlorine decay by dividing the time into three stages; an initial rapid reactions period ($t < 5$ minutes); a second-order reaction (5 minutes $< t <$ 5 hours); and a third period defined by a first-order reaction ($t >$ 5-hours).

Clark & Sivaganesan (1998) also developed a second order model for chlorine decay based on the concept of competing reacting substances and the assumption that the balanced reaction equation can be represented by:

$$aA + bB \rightarrow pP \qquad (2.9)$$

Where A & B are the reacting substances, with ‘a’ and ‘b’ being the proportions of each, respectively. P is the product of the reaction, with ‘p’ the stoichiometry constant.

The model assumes that the velocity of the reaction is proportional to the concentrations of both reacting species, and through mathematical calculations culminates in the following expression for calculating the chlorine concentration at a time, t:

$$C_A = \frac{C_{A0}(1-K)}{\left[1-K\exp(-ut)\right]} \qquad (2.10)$$

Where: C_A = Concentration of free chlorine at time, t

K = $\lambda C_{B0} / \gamma C_{A0}$ = a dimensionless constant

C_{A0} = Initial concentration of chlorine, C_A

C_{B0} = Initial concentration of substance, C_B

u = A rate constant

t = Time (hours)

A first-order model with respect to chlorine reactions is included in most network analysis water quality models due primarily to its simplicity and adoption in numerous studies (Rossman *et al*., 1994; Vasconcelos *et al*., 1997; Gang *et al*., 2002). Work undertaken at the UoB (Powell, 1998; Hua, 2000; Hallam, 1999) all concluded that for the distribution systems investigated in the STW region that a first-order model with respect to chlorine was adequate, although its application to various waters with different qualities may not be warranted.

2.6 Parameters affecting bulk chlorine decay

It is well documented that a number of parameters will affect bulk chlorine decay. Organic and inorganic content, temperature, initial chlorine concentration, and pH have been highlighted as being of particular significance.

2.6.1 Organic concentration

Natural organic matter (NOM) is ubiquitous in surface and ground water sources, and usually exists at concentrations between 2-10 mg/l (Bolto *et al.*, 2002), although much higher levels are sometimes found depending on the watershed characteristics (Garcia, 2005). For most waters, in particular water in distribution systems, the reactions of chlorine with organic matter makes up the majority of the chlorine demand (Clark & Bouton, 1998). A relationship between organic matter concentration and chlorine decay would therefore be expected.

Characterisation of NOM is typically undertaken on either bulk NOM material or fractionated NOM material. The advantage of bulk water studies is that 100 % of the NOM is present in an unaltered state, therefore making results from such studies directly applicable for the specific reaction conditions and water. The disadvantage is that the factors that effect the reactions of specific types of NOM cannot be identified or understood (Goslan, 2003). The study of isolated NOM fractions can provide operationally defined samples for examination of NOM behaviour, however, synergistic effects are often lost (Hwang *et al*., 2001).

Total organic carbon (TOC) is the most widely adopted surrogate measure of organic content in water and a number of models have been proposed relating the parameter to the bulk chlorine decay constant (K_B) (*e.g.* Jadas-Hécart *et al*., 1992; AWWARF, 1996; Kiene *et al*., 1998; Powell, 1998; Hallam, 1999; Hua, 1999; Courtis, 2003; Vieira *et al*., 2004). Work published by the AWWARF (1996) and Powell (1998) suggested a linear relationship, whereas Kiene *et al*. (1998) stated the following first order relationship concerning both TOC and temperature:

$$K_B = a \cdot TOC \cdot \exp\{-b/(T+273)\} \qquad (2.11)$$

Where: K_B = Bulk chlorine decay constant (l/hr)

TOC = Total organic content (mg/l)

T = Temperature (°C)

a & b = Constants

Subsequent work illustrated that if reduced beyond a certain level of TOC, a linear relationship would suggest no chlorine would react, which in practice is unlikely. Hallam (1999) and Hua (2000) suggested a more pragmatic approach is to use a power function, where both the TOC concentration and bulk decay would be expected to tend to zero as the number of reactants available decreased. The following relationship was adopted by both researchers and subsequently by Courtis (2003):

$$K_B = \psi \, TOC^{\phi} \qquad (2.12)$$

Where: K_B = Bulk chlorine decay constant (l/hr)

TOC = Total organic content (mg/l)

ψ and ϕ = Constants determined by experimentation

2.6.2 Inorganic concentration

Inorganic components are traced to various minerals and other substances in the water derived from non-biological sources. These substances may occur naturally in the water or may be anthropogenic in nature. During chlorination, in the case of inorganic compounds, fast reactions with ammonia (NH_3), halides (Br^- and I^-), SO_3^{2-}, CN^-, NO_2^-, As (III) and Fe(II) with HOCl have been reported (Deborde & von Gunten, 2008).

Of particular importance, in terms of chlorine and disinfection efficiency, are the reactions involving ammonia or amino-nitrogen groups. The reactions between HOCl and natural ammonia ions contained within the water (due to the breakdown of nitrogen based compounds) yields, successively, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (more commonly known as nitrogen trichloride, NCl_3). The simplified stoichiometry of chlorine-ammonia reactions are as follows:

Monochloramine: $NH_3 + HOCl = NH_2Cl + H_2O$ (2.13)

Dichloramine: $NH_2Cl + HOCl = NHCl_2 + H_2O$ (2.14)

Trichloramine: $NHCl_2 + HOCl = NCl_3 + H_2O$ (2.15)

These competing reactions are primarily dependant and controlled to a large extent by the chlorine: ammonia nitrogen ratio. Temperature, pH and contact time also play a significant role. Only once the chlorine demand of the ammoniacal nitrogen has been satisfied will the resultant free chlorine residual be proportional to the dose. This occurs at what is known as the ‘breakpoint’ in the addition of free chlorine, and requires approximately eight parts of chlorine to one part ammonia. Ammonia is sometimes added to the water at a WTW to ensure the formation of combined chlorine, a practice termed chloramination (see Appendix A.3).

2.6.3 Temperature

It is widely acknowledged that nearly all chemical reactions increase with temperature, with the Arrhenius equation being widely accepted to describe the relationship (Coulson & Richardson 1964; Faust & Aly, 1983; Jadas-Hécart *et al.*, 1992; Powell, 1998):

$$K = F \cdot \exp\{-E/R(T+273)\} \qquad (2.16)$$

Where:
K = The rate constant
F = Frequency factor (units dependant on reaction order)
E = Activation energy (J/mol)
R = Ideal gas constant (8.31 J/mol ºC)

A very approximate rule is that reaction rates double for every 10°C rise in temperature (Fair, 1965). This is equivalent to a value of 5750°C for E/R in the Arrhenius equation for a temperature rise from 10 to 20°C. Over an annual cycle, water temperatures in UK water supply systems typically vary between 5 and 25°C. Hence, according to this rule of thumb, a quadrupling of the decay rate between winter and summer may be expected.

The impact of temperature upon bulk decay has been discussed by a number of authors (Fair, 1965; Faust & Aly, 1983; Zhang *et al.*, 1992, Jadas-Hécart *et al.*, 1992; Gallard & Gunten, 2002; Vieira *et al.*, 2004), although only a few have tried to define the relationship quantitatively. Work published by the AWWARF (1996) described the relationship of temperature and TOC on chlorine decay rates via the following expression:

$$k_0 = A_2 TOC \exp\left[-\frac{E}{R\theta}\right] \qquad (2.17)$$

Where: TOC = Total organic carbon concentration (mg/l)

A_2 = Constant (estimated at 1.8×10^6 l/mg hr)

E/R = Constant (estimated at 6050 °Kelvin)

Note the E/R part of this expression is equivalent to the ‘b’ in the equation developed by Kiene *et al.* (1998) (Equation 2.11).

2.6.4 Initial chlorine concentration

Previous experimental studies have shown an inverse relationship between K_B and C_0, when tests were conducted on the same waters under identical laboratory conditions (Dharmarajah *et al.*, 1991; Zhang *et al.*, 1992; UKWIR, 1998; Powel, 1998; Hua, 1999; Hallam, 2000; Courtis, 2003; Vieira *et al.*, 2004; Warton, 2006). Powell (1998) and Hallam (1999) suggested an inverse relationship of the following form:

$$K_B = \gamma . C_o^{\eta} + \sigma \qquad (2.18)$$

Where: K_B = Bulk chlorine decay constant (l/hr)

C_0 = Initial chlorine concentration (mg/l)

γ, η, σ = Initial chlorine experimental constants

2.6.5 pH

Given the sensitivity of chlorine speciation to pH (section 2.3) it is surprising that a relatively small amount of work has been carried out on the influence of pH upon chlorine decay. The main reason for this is that pH control at most WTW's chlorination points results in relatively constant pH levels.

2.7 Wall chlorine decay

Research has shown that the bulk chlorine decay rate is smaller than the chlorine decay observed in the distribution system (Wable *et al*., 1991; Clark *et al*., 1993; AWWARF, 1996; Powell, 1998; Hallam, 2000; Al-Jasser, 2007; Lee *et al*., 2007; Yeh *et al*., 2008). Therefore aside from bulk consumption, chlorine also decays due to interactions with pipe and tank walls and fittings. This 'wall decay', which includes corrosive reactions with the wall material itself, with adhering biofilms and with accumulated sediments, is mostly a function of the mass transfer of chlorine from the bulk water to the pipe walls, pipe material, diameter, age, inner coating and the presence of attached biofilms (Vasconcellos *et al*., 1997; Kiene *et al*., 1998; Vieira *et al*., 2004; Warton *et al*., 2006; Al-Jasser, 2007).

A number of models have been suggested to account for the more complex chemical reactions that take place within distribution system pipe networks. The simplest model has been to fit the first order decay equation to the in-situ decay in pipes (Wable *et al*., 1991; Zhang *et al*., 1992; Biswas *et al*., 1993; Rossman *et al*., 1994; Kiene *et al*., 1998; Powell, 1998; Hallam, 1999). Most of these models have used constants to compensate for inaccuracies in flow and chlorine measurement, to help explain the variations between observed and modelled chlorine concentrations.

AWWARF (1996) defined the overall chlorine decay constant (K_T) to be a sum of the first order bulk decay constant and the effective wall decay constant:

$$K_T = K_B + K_W \qquad (2.19)$$

Where: K_T = First order decay constant (l/hr)

K_B = Bulk chlorine decay constant (l/hr)

K_W = Wall chlorine decay constant (l/hr)

This approach has the advantage of being simple and with the decay constants having the same units allows for straightforward comparison.

Rossman *et al*. (1994) similarly assumed first order equations for both bulk and wall decay. They developed a mass-transfer coefficient to account for the radial transport and estimated the wall consumption. The equation was incorporated into the EPANET hydraulic model in the following form:

$$K = K_B + K_{wEPA} \, . \, K_{fEPA} / [R_H \, (K_{wEPA} + K_{fEPA})] \qquad (2.20)$$

Where: K = First order decay constant (hr^{-1})

K_B = Bulk demand first order decay constant (hr^{-1})

K_{wEPA} = EPANET's wall decay constant (m/hr)

K_{fEPA} = EPANET's mass transfer constant (m/hr)

R_H = Hydraulic radius (m)

The mass transfer coefficient is a function of the pipe diameter and water velocity, being particularly sensitive at low values (less than 75mm diameter or 0.02 m/s velocity) (Powell 1998). This suggests that over a typical range of velocities and pipe diameters, the EPANET equation would give similar results to the basic AWWARF (1996) equation discussed previously (2.19).

Vasconcelos *et al*. (1996) found a zero order wall decay kinetic reaction was effective for characterising the wall decay, but also indicated that the first order model might be better. They suggested that in metallic pipes the wall demand is independent of the chlorine concentration and therefore an adaptation of the EPANET equation was required. DiGiano & Zhang (2005) also concluded that a zero-order overall kinetic model was well suited for describing the overall chlorine decay in a heavily tuberculated cast iron pipe, whereas, a first order overall kinetic model was found suitable for new cement lined ductile iron (CLDI) pipes.

A summary of chlorine wall decay constants reported in the literature and the summary of test conditions are provided in Table 2.1.

2.8 Disinfection by-products (DBPs)

Work by Rook (1974), in Holland, and Bellar *et al.* (1974), working separately on several water supplies in USA, reported on the identification of the first DBPs, chloroform and other THMs formed in chlorinated drinking water. In 1976, the US Environmental Protection Agency (USEPA) published the results of a national survey that showed that chloroform and other THMs were ubiquitous in chlorinated drinking water. Also in 1976, the US National Cancer Institute published results linking chloroform to cancer in laboratory animals (NCI, 1976). As a result, an important public health issue was born (Richardson, 2003).

Although numerous DBPs have been reported in the literature since that time, with more than 700 confirmed species to date (Ates *et al*., 2007; Richardson *et al*., 2007; Chen *et al*., 2008), only a small number have been addressed in either quantitative or health effects studies. The DBPs that have been quantified in drinking water are generally present at sub-μg/l (ppb) or low-to-mid-μg/l levels. Approximately 50% of the total organic halide (TOX) formed during the chlorination of drinking water and more than 50% of the assimilable organic carbon (AOC) formed during ozonation of drinking water is still not accounted for and nothing is known about the potential toxicity of many of the vast number of DBPs present in drinking water (Richardson *et al*., 2007).

The principal by-products of disinfection are listed in Table 2.2 (*as cited in* Singer, 1994). The concentrations of each species of DBP will vary according to both water source and the treatment of the water. Research, such as that undertaken by Krasner *et al*. (1989), Neiminski *et al*. (1993) and Lee *et al.* (2004), has shown that detected on a weight basis, the largest fraction of DBP to be found in treated water are THMs, accounting for approximately 50% of all halogenated DBP. The next largest fraction being haloacetic acids (HAAs), with their concentration on average being half that of THMs (Krasner *et al.*, 1989). As this project deals primarily with THMs, the rest of this literature review will focus upon these compounds.

2.9 Trihalomethanes

Trihalomethanes (THMs) are halogen-substituted single-carbon compounds with the general formula CHX_3, where X may be chlorine, bromine, fluorine, or iodine, or combinations thereof (Latifoglu, 2003). THMs result primarily from reactions between chlorine or bromine and naturally occurring organic compounds via the “classical” haloform reaction mechanism (Adin *et al.*, 1991). The general reaction leading to the formation of THMs during chlorination can be expressed as follows:

$$HOCl + Br^- + I^- + NOM \rightarrow THMs\ and\ other\ Halogenated\ DBPs \quad (2.21)$$

The four THMs that are found in measurable quantities and which compose TTHM (total trihalomethane) are chloroform ($CHCl_3$), chlorodibromomethane ($CHClBr_2$), bromodichloromethane ($CHBrCl_2$) and bromoform ($CHBr_3$). All THMs are relatively to extremely volatile and slightly water soluble, with a solubility of less than 1 mg/ml at 25°C (WHO, 2005). In most surface water systems chloroform is by far the most prevalent THM (Rodriguez *et al.*, 2003; Baytak *et al.*, 2008), but higher bromide concentrations can lead to a significant shift towards levels of brominated THMs, as these account for three of the four components that comprise TTHMs.

2.9.1 Regulations and limits

Through toxicity, neurotoxicity, carcinogenicity, mutagenicity and tetrogenicity testing, guidelines have been set by the World Health Organisation (WHO) on the health implications of DBPs in drinking water (Komulainen, 2004). The European Union recently amended the regulated concentration of TTHMs in member states to 100 µg/l from 150 µg/l (prior to the end of 2008) (Directive 80/778/EC). Individual member states, however, are allowed to set their own regulations provided that they are not less stringent than those set in the Directive (Teksoy *et al*., 2008). The current standard in the UK changed from a previous three-month rolling mean to an absolute concentration of 100 µg/l in December 2003 (Defra / DWI, 2008).

Future regulations are likely to focus more on individual (rather than combined) concentrations of DBPs as the ever-increasing amounts of epidemiological studies indicate different individual species may have different health effects.

2.9.2 Epidemiological studies into THMs

Epidemiological evaluation of chlorination by-products in drinking water commenced soon after chloroform was discovered in 1974 in drinking water supplies and has continued to the present day (IARC, 1976, 1991; Fawell, 2000; Moudgai *et al*., 2000; Villanueva *et al*., 2004; McDonald & Komulainen, 2005; WHO, 2005; Bove *et al*., 2007; Wang *et al*., 2007). A collection of the findings from these studies is provided in Appendix B.

2.10 THM formation and precursors

The distribution of each species of THM will vary according to water source, the treatment processes and conditions operated at the water treatment works, and the nature of the distribution system. The key factors that can influence THM formation are pH, organic concentration and matrix, bromide concentration, free chlorine concentration and contact time.

2.10.1 pH

A higher pH leads to an increase in the rate and hence, quantity, of THMs formed (Rook, 1974; Trussell & Umphres, 1978; Reckhow & Singer, 1985; Krasner *et al*., 1989; Adin *et al*., 1991; Hua, 1999; Liang & Singer, 2003). Trussell & Umphres (1978) postulated that THM formation involves a hydrolysis step that is facilitated at higher pH. The increase in THMs was shown by Stevens *et al*. (1995) to be counterbalanced by a decrease in other DBPs, including haloacetic acids (HAAs).

2.10.2 Organic matrix

NOM is a prerequisite to THM formation (Kitis *et al*., 2001; Parsons *et al*., 2004). NOM can be broadly divided into two fractions; humic substances, which are composed of fulvic and humic acids, and non-humic substances, which include carbohydrates, hydrocarbons, lipids and amino acids (Karnik *et al.*, 2005; Fabris *et al*., 2008).

As a result of its heterogeneous and undefined character, the amount of NOM is typically measured through surrogate parameters such as TOC, dissolved organic carbon (DOC), or ultraviolet absorbance at 254 nm (UV_{254}). Another measure commonly applied is the specific ultraviolet absorbance (SUVA), which is equal to the UV absorbance divided by the dissolved organic carbon concentration. This value has also been found to be a good indicator for the humic content of the water, which according to research by Owen *et al.* (1993), Krasner (1999) and Reckhow *et al.*, (2004) has a higher propensity to form DBPs than the non-humic fraction.

TOC has traditionally been used as a measure of THM precursor material. Research relating the two (Fleischacker & Randtke, 1983; Carlson & Hardy, 1998; Powell, 1998; Hua, 1999; Golfinopoulos & Arhonditisis 2002; Courtis, 2003) all reach a similar conclusion, that an increase in the organic matrix in the water increases both the rate and extent to which THMs form. TOC does cover a large and varied number of different compounds; therefore it is not always an accurate surrogate for THM formation, as demonstrated by Powell (1998) for TOC concentrations below 1.3 mg/l. There have also been attempts to incorporate the use of UV_{254} absorbance as a measure of precursor material with varying success (Reckhow *et al.*, 1990; Clark *et al.*, 1994; Kitis *et al.*, 2001; Banks *et al.*, 2002).

Recent research, aimed at improving the knowledge of precursor material, has attempted to identify relationships between individual components of NOM and THM formation (Gang *et al.*, 2003a; Parsons *et al.*, 2004; Kim & Yu, 2005). Liang & Singer (2003) identified that the hydrophobic fractions always gave higher THMs and HAAs formation potentials than their corresponding hydrophilic fractions in the same sample waters. Reckhow *et al.* (1990)

reported an increase in halogenated DBP formation with an increase in the activated (defined as electron rich) aromatic content of NOM.

Research has shown algal biomass and extra-cellular products can act as THM precursor material (Hoehn *et al*., 1980; Wardlow *et al*., 1991; Graham *et al*., 1998; Reckhow *et al*., 2004). This is particularly problematic for source waters extracted from eutrophic reservoirs, which can lead to potentially elevated THM concentrations at certain times of the year (Graham *et al*., 1998).

2.10.3 Temperature and seasonal variation

Although there have been relatively few studies that have investigated how temperature implicitly affects DBP formation, it is widely acknowledged that an increase in temperature increases DBP formation (Kavanaugh *et al.,* 1980; Krasner *et al*., 1989; Rodriguez & Serodes, 2001; Kim *et al.*, 2002; Toroz & Uyak, 2005). Through modelling of THM formation, Kavanaugh *et al.* (1980) found that the rate constant for the formation of THM exhibited an Arrhenius-type relationship with temperature, doubling with every 10°C increase between 0°C and 30°C. Engerholm & Amy (1983) expanded on this by demonstrating that temperature increased not only the rate, but also the extent to which THMs can form.

Higher temperatures will generally increase the rate of reaction. Consequently, THM formation increases through the larger doses of chlorine required. Higher temperatures also mean a higher rate of hydrolysis (where water molecules split into hydrogen and hydroxide ions), which leads to a faster break up of aromatic bonds, allowing further halogenation and a higher formation of DBPs (Garcia *et al*., 2005).

Temperature effects on THM formation are particularly pronounced in surface waters, as demonstrated by the recent work of Courtis (2003) and Roberts (2004) on Melbourne and Bamford WTWs, respectively. Both researchers found temperature to be the dominant factor during summer months. Krasner (1999) analysed the data of 35 water treatment utilities in the United States and also found that the mean THM formation was highest in the summer and lowest in the winter.

In addition to the direct effects of temperature, seasonal variations in the characteristics and composition of organic precursors were also found to be of significance in Krasner's (1999) and others studies (Rodriguez *et al*., 2001; Toroz & Uyak, 2005; Rodriguez *et al*., 2007; Uyak *et al*., 2008). Further understanding of the seasonal changes in organic matter character and their reactivity with treatment chemicals would aid in better optimization of the treatment processes and a more consistent water quality (Uyak *et al*., 2008).

2.10.4 Bromide concentration

With respect to the brominated THM's, the formation of hypobromous acid (HOBr) is of notable importance:

$$HOCl + Br^- \quad = \quad HOBr + Cl^- \qquad (2.22)$$

Hypochlorous acid / hypochlorite ion oxidises the available bromide in the water to form hypobromous acid (HOBr) / hypobromite ion (OBr^-) (Singer, 1999; Chang *et al*., 2001; Ates *et al*., 2007). By analogy with HOCl and OCl^-, both HOBr and OBr^- react with NOM to form a mixture of brominated and mixed chloro-bromo derivatives. Although chlorine is more reactive than bromide (having a electronegativity value of 3.16 in comparison to 2.96 on the Pauling scale), of the compound formed after oxidisation, HOBr is 25 times more reactive than its counterpart HOCl (Chang *et al.*, 2001). However, if chlorine is in excess and the amount of available bromide is low, chloroform will be the dominant species of THM formed. The formation of brominated THMs is therefore a function of the Br_2: NOM ratio and Br_2: Cl_2 ratio (Summers *et al*. 1993; Roberts, 2004).

Over recent years the interaction of bromide within the disinfection process and THM speciation have received more interest (*e.g.* Nokes *et al.,* 1999; Ichihashi *et al.,* 1999; Chang *et al*., 2001; Elshorbagy *et al*., 2000; Roberts, 2004; Westerhoff *et al.*, 2004; Ates *et al*., 2007; Sohn *et al.,* 2007). This research has been carried out because of the importance of the molecular weights of the four species (Table 2.5) and the effects of regulatory influences, with the possibility of limits for individual THMs in the future. Bromine (atomic weight of 79.9) is much heavier than chlorine (atomic weight of 35.5), thus the concentration of the correlated bromoform will be approximately twice that of the chloroform. Brominated organic by-products are also suspected to be more harmful to health than chlorinated analogues (Bull & Kopfler, 1991; Nobukawa & Sanukida, 2001; Richardson, 2003; Bove *et al*., 2007). For example, bromodichloromethane has been reported to pose a higher cancer risk than chloroform (Krasner *et al*., 1996) and the risk of rectal cancer has been shown recently to be associated specifically with levels of bromoform (Bove *et al*., 2007) (see Appendix B for a summary of the health effects).

The bromine incorporation factor (BIF) provides a useful measure to facilitate the discussion of the various mixtures of THMs that could be formed in the presence of bromine and its affiliated compounds. Defined by Gould *et al.* (1981) as the molar THM concentration as bromide divided by the total molar THM concentration, it can be calculated by following expression:

$$N = \frac{\sum_{n=0}^{3} n(CHCl_{3-n}Br_n)}{\sum_{n=0}^{3} CHCl_{3-n}Br_n} \qquad (2.23)$$

Where the quantity of each THM compound is on a molar basis. When only chloroform is present, N = 0; when only bromoform is present, N = 3. Accordingly, this factor characterizes in one number the molar incorporation of bromine into the TTHM, compared with using four concentrations to define THM species.

Rathburn’s (1996) study of chlorinated river waters in the USA, indicated that treatment conditions designed to minimize the total trihalomethane concentration (via organics removal) will most likely increase the extent of bromination, due to the increase in the Br : NOM ratio. It was also shown that the bromine incorporation factor increased as the bromide concentration increased, and decreased as the pH, initial free chlorine and DOC concentration increased. Sohn *et al.* (2007) also showed BIF to increase with the ratio of bromide : DOC and observed an increase with a rise in temperature.

2.10.5 Alternative sources of precursor material

In addition to natural sources of NOM, anthropogenic sources of organic matter exist, which can contribute towards the formation of DBPs. Feige *et al*. (1980) demonstrated certain water treatment chemicals to be a source of organic matter that led to the formation of DBPs, whereas the release of industrial chemicals and minerals into the environment is a largely unknown contributor to DBP formation. Potentially, foodstuffs and bodily fluids can also act as DBP precursors.

2.10.6 Free chlorine

The presence of free chlorine is a prerequisite to THM formation. It is generally accepted that the THM formation increases with increasing chlorine dose (Adin *et al*., 1991). However, it appears that chlorine residuals way in excess of chlorine demand have little impact on increasing the rate of THM formation (Trussell & Umphres, 1978; Fleischacker & Randtke, 1983). THM formation increases with increasing chlorine dosage up to a point where the reaction is no longer chlorine limited. Beyond this point the reaction is likely to be TOC limited. Carlson & Hardy (1998) demonstrated that with a chlorine : TOC ratio of less than 1, chlorine had the greatest affect on THM formation. Above this ratio it was found that there was little change in amounts of THM formed.

Singer (1994) indicated that with an increasing chlorine dose and residual, formation of haloacetic acids becomes greater than THM formation. A similar finding was reported by

Reckhow and Singer (1985). Depletion of the free chlorine residual ceases THM and HAA formation, however, limited formation of some other DBPs continues due to hydrolysis reactions (Singer, 1994; Nikolaou *et al.*, 1999; Liang & Singer, 2003).

The reaction of chlorine with water in forming THMs can be divided into three sections, as described by Kruitof (1998), Courtis (2003) & Roberts (2004). In the first, chlorine will suppress the demand imposed by the inorganic matrix of the water, resulting in very little THM being formed. The bulk of THM will be formed in the second section when chlorine reacts with the "fast reacting" organics. Finally, in the third section, chlorine will react with the "slow reacting" organic matter producing THM at a slower formation rate.

2.11 Prediction and modelling of THM formation

This section provides an overview of previous modelling work on THM formation. Due to the complexity and uncertainty of reactions between chlorine and the organic matrix, successful analytical-mechanistic-kinetic models of THM formation have not yet been developed. Therefore, the majority of models are based around empirical or semi-empirical kinetic equations derived from linear and non-linear regression analysis. Detailed reviews of these models may be found in Amy *et al*. (1987); Clark & Sivaganesan (1998); Clark *et al*. (2001); Sadiq & Rodriguez (2004); Roberts (2004); Chowdhury *et al*. (2009).

The success of THM formation models has been variable, and in general has comprised of a multiple parameter functions of the following form, proposed by Amy *et al*. (1987):

$$TTHM = k \times (t)^{a} \times (Co)^{b} \times (TOC)^{c} \times (\theta)^{d} \times (pH)^{e} \times (UV_{254})^{f} \times (Br)^{g} \quad (2.24)$$

Where:

TTHM = Total trihalomethanes

k = Reaction constant

t = Time

C_0 = Initial chlorine concentration at t = 0

TOC = Total Organic Carbon (mg/l)

θ = Temperature (˚C)

pH = pH

UV_{254} = UV_{254} absorbance

Br = Bromide concentration (mg/l)

a – g = Reaction constants determined by experiments

The first attempt at modelling THM formation was presented by Trussel *et al.* (1978), who reviewed the effect of pre-ozonation, bromide concentration, pH and chlorine dose on the formation of THMs in natural waters. They proposed a differential rate expression relating the rate of THM production to chlorine residual to the first power and to the precursor concentration to the m^{th} power. TOC was used as a measure of precursor concentration and ‘m’ was assumed to be 3. The authors concluded that that there are a number of important factors in describing the formation of THMs including; the nature of aquatic humus, the influence of pre-ozonation, the influence of bromide, pH and chlorine dose. Although a good fit was observed to the experimental data, the author deemed the relationship unlikely and suggested further work needed to be undertaken.

Engerholm & Amy (1983) conducted an investigation that looked at the formation of chloroform from humic acid as a function of time, where the rate was tested under several various experimental conditions. Although the experiments neglected the effects of bromide, the concentration of TOC, ratio of initial chlorine concentration to TOC, reaction pH and temperature, were all investigated. The overall model incorporated a series of sub-models, which were used to evaluate the effects of important parameters, and was presented in the following form:

$$CHCl_3 = k_1 \cdot (TOC)^{z1} \cdot (Cl_2 / TOC)^{z2} \cdot (t)^{z3} \qquad (2.25)$$

Where: $CHCl_3$ = Chloroform

TOC = Total organic carbon

Cl_2 = Free chlorine concentration

z_1, z_2, z_3 = Empirical constants to be determined experimentally

k_1 & k_2 = Reaction constants related to pH and temperature

The above expression (2.25) was later expanded by Amy *et al.* (1987) into its more recognisable form (2.24) with the inclusion of such parameters as temperature, pH, bromide and UV_{254}. The expanded model assumed that a chlorine residual is maintained throughout a 168-hour reaction period and that TTHMs continuously increase with time. By transforming the variables into natural log forms and using multiple regression analysis, an expression was found relating the natural log of TTHM formation as a function of the natural logs of time, temperature, initial chlorine concentration, the product of UV absorbance and TOC concentration, bromide concentration and pH. By taking anti-logs of both sides of the equation, the following expression for the direct calculation of TTHM was born:

$$\mathrm{TTHM} = 0.00325 \times (t)^{0.252} \times (Co)^{0.517} \times (\mathrm{TOC} \times \mathrm{UV}_{254})^{0.378} \times (\theta)^{0.985} \times (\mathrm{pH} - 2.6)^{0.640} \times (\mathrm{Br} + 1)^{0.0536} \qquad (2.26)$$

Where:
TTHM = Total trihalomethanes
t = Time (hrs)
C_0 = Initial chlorine concentration (mg/l)
TOC = Total Organic Carbon (mg/l)
UV_{254} = UV_{254} absorbance
θ = Temperature (°C)
Br = Bromide concentration (mg/l)

As stated at the beginning of this section, this model formed the basis for the majority of THM formation models that followed and is the single most extensively cited reference in THM modelling. It has also been incorporated into the WRc OTTER water treatment modelling package (Bridge, 2005).

Clark *et al.* (1994), while researching data collected from two distribution system sources located in North Marin Water District in California, reported that UV_{254} absorbance and TTHM were closely related. Regression analysis determined the following relationship (with an R^2 of 0.975):

$$TTHM = 2.056 + 1648.2\ UV_{254} \qquad (2.27)$$

Complementing Clark's (1998) work on chlorine decay, Clark and Sivaganesan (1998) developed an equation to predict chlorine decay and THM formation based on chlorine consumed. Developed using regression analysis of experimental data of humic acids, the model assumes THM formation to be a function of TOC, temperature, initial chlorine residual and pH. Bromide and the formation of brominated THMs were neglected in the model. The following equation was presented:

$$TTHM = DC_0\left[1 - \frac{1-K}{1-K\exp(-ut)}\right] \qquad (2.28)$$

Where: C_0 = Initial chlorine concentration

D & K = Dimensionless constants

u = M (1-K)

The parameters D, K and M are based on initial chlorine decay, TOC, pH, and temperature and are calculated by the following set of equations:

$$K = e^{0.32} \text{ x } (C_0)^{-0.44} \text{ x } (TOC)^{0.63} \text{ x } (pH)^{-0.29} \text{ x } (\sigma)^{0.14} \qquad (2.30)$$

$$D = e^{1.49} \text{ x } (C_0)^{-0.48} \text{ x } (TOC)^{0.18} \text{ x } (pH)^{0.96} \text{ x } (\sigma)^{0.28} \qquad (2.31)$$

$$U = M(1-K) \qquad (2.32)$$

$$Ln(M) = -2.46 - (0.19 \cdot TOC) - (0.14 \cdot pH) - (0.07 \cdot \sigma) + 0.01(\sigma \times pH) \quad (2.33)$$

Where: TOC = Total organic carbon

pH = pH

σ = Temperature

Clark & Sivaganesan (1998) verified this equation using both field and laboratory data from the study by Vasconcelos *et al*. (1997) and from laboratory data collected by the WSWRD of EPA (Clark *et al*., 2001; Sadiq & Rodriquez, 2004).

Recent work by Hua (1999) and Roberts (2004) has sought to develop an empirical equation in line with that proposed by Amy *et al*. (1987). Hua (1999) investigated three STW water treatment works over a three year period to assess the change in water quality parameters and model TTHM formation, specifically through the works. Initial studies omitted bromide and UV_{254}, as without them, R^2 values were significantly improved (Hua, 1999). The following equation was then applied to the three works:

$$TTHM = Q \times (t)^a \times (C_0)^b \times (TOC)^c \times (\sigma)^d \times (pH)^e \quad (2.34)$$

Where: TTHM = Total trihalomethanes

Q = THM formation index constant for water at a point in treatment stage.

t = Time

C_0 = Initial chlorine concentration

TOC = Total organic carbon

θ = Temperature

pH = pH

a-g = Reaction constants to be determined experimentally

Results suggested that TTHM formation was closely linked to chlorine consumed, confirming claims made by Trussell *et al.* (1978), Kavanaugh *et al.* (1980) and Clark (1998). This led to a simplified model using the following equation:

$$TTHM_t = K_{TC} \cdot (C_0 - C_t) \qquad (2.35)$$

Where:

TTHM = Total trihalomethanes concentration at time, t (µg/l)

K_{TC} = µg/l TTHM per mg/l chlorine

C_0 = Initial chlorine concentration (mg/l)

C_t = Chlorine concentration at time, t (mg/l)

The work concluded that with the exemption of significant quantities of bromide, a K_{TC} of 45 µg/l TTHM per mg/l Cl would not change at a specific WTW. It also suggested that the K_{TC} value was not affected by temperature or variation in TOC. Clark & Sivaganesan (1998), however, reported that over a longer test period TOC and temperature would be likely to have more of an influence on the K_{TC} value.

Courtis (2003) extended this work to model TTHM formation in both the works and in distribution, also assuming that TTHM formation is proportional to chlorine consumed. Analysis of results from chlorine decay kinetics through water treatment works and distribution system confirmed the figure of 45 µg/l per mg/l free Cl_2 for K_{TC} at the end of the contact tank. It was suggested that a figure of 27 µg/l per mg/l Cl_2 would be more appropriate for THM formation prediction after the first re-chlorination. This is in accordance with work undertaken by Kruitof (1999) on chlorinating Biesosch water in the Netherlands (see section 2.10.6).

Uyak *et al*. (2005) studied the formation of THM at the Kagithane WTW in Istanbul. Routine measurements of THM, TOC, pH, temperature and chlorine dose over a 12-month sampling program, were used to develop a multiple linear regression model for the prediction of THM in raw water. This took the following form:

$$THM = 0.0707 \cdot (TOC + 3.2)^{1.314} \cdot (pH-4.0)^{1.496} \cdot (D-2.5)^{-0.197} \cdot (T+10)^{0.724} \quad (2.36)$$

Where: THM = Total trihalomethane concentration (µg/l)

TOC = Total organic carbon concentration (mg/l)

D = Chlorine dose (mg/l)

T = Temperature (°C)

Both pH (R^2 ~ 0.96) and temperature (R^2 ~ 0.92) were found to be the parameters of the highest statistical significance as predictors for TTHM occurrence. Although the model proved accurate in its application to the chlorination of raw waters, it does not represent treated water characteristics and chlorination. It also does not consider reaction time as an explanatory variable.

Hong *et al*. (2007) found bromide was a key factor in determining bromine incorporated THM formation and consequently the speciation of THMs. Their study of THM formation due to the chlorination of Dongjiang River water (a major source of drinking water supply for Hong Kong), followed an orthogonal design, which allowed for the variation of only one parameter at a time while other parameters maintain a designated 'baseline' condition. The following set of equations for determining both TTHM and individual THM species were developed from the analysis:

$$\text{TTHM} = 10^{-1.375} \,.\, t^{0.258} \,.\, (D/DOC)^{0.194} \,.\, pH^{1.695} \,.\, T^{0.507} \,.\, (Br^{-})^{0.218} \tag{2.37}$$

$$CHCl_2Br = 10^{-3.201} \,.\, t^{0.297} \,.\, pH^{2.878} \,.\, T^{0.414} \,.\, (Br^{-})^{0.371} \tag{2.38}$$

$$CHCl_3 = 10^{-1.375} \,.\, t^{0.258} \,.\, (D/DOC)^{0.194} \,.\, pH^{1.695} \,.\, T^{0.507} \,.\, (Br^{-})^{0.218} \tag{2.39}$$

Where:
TTHM = Total trihalomethane concentration (µg/l)
DOC = Dissolved organic carbon concentration (mg/l)
T = Temperature (°C)
Br^- = Bromide (µg/l)
$CHCl_2Br$ = Bromodichloromethane (µg/l)
$CHCl_3$ = Chloroform (µg/l)

Akin to the study by Uyak *et al*. (2005), this study concentrated on raw water characteristics and hence its application to the representation of treated water characteristics is thus limited.

2.12 Options for the reduction / removal of THMs & DBPs

With more stringent legislation for DBPs on the horizon, there is increasing pressure on the water industry to improve the efficiency of existing processes or to install more advanced systems to help combat the problem. Nonetheless, as stated in the WHO guidelines (2005), any method of control employed must not compromise the overall effectiveness of water disinfection. This section highlights a number of options available for controlling DBP concentrations, some of which are more feasible than others.

2.12.1 Disinfection dose point

The point at which a disinfectant is added in the treatment stream has a large impact on DBP concentrations. Where there is a known problem with DBPs the disinfection stage should be as far down the treatment process stream as possible, consistent with achieving effective disinfection. The move away from front end chlorination at STW surface WTW has brought about a significant reduction in THM levels and has been the main reason why the Company has not exceeded the 100 μg/l compliance concentration (in regulatory tests) at any of their surface water works in recent years.

2.12.2 Removal of DBP precursors

It is clear that the lower the concentration of precursors at the point of disinfection the better. Clearly, in respect of the organic parameters, attempts to maximise their removal at the source is the preferred option. While ecologists and hydrologists have explored the origin, transport and fate of organic carbon in surface waters (*e.g.* Hope *et al*., 1994; Graham *et al*., 1998; Aitkenhead *et al*., 1999), little has been done to understand the origin and behaviour of specific organic DBP precursor compounds (Reckhow *et al*., 2004).

The removal of NOM and THM precursors in conventional coagulation has been demonstrated in laboratory research, pilot- and full-scale studies. Numerous studies have shown that organic carbon exhibits a wide range of responses to treatment with aluminium and iron salts (*e.g.* Owen *et al*., 1993; White *et al*., 1997; Fabris *et al*., 2003; Goslan, 2003; Singer & Liang, 2004; Teksoy *et al*., 2008). Optimisation of the clarification stages in surface water works is key to DBP precursor removal, with particular attention being paid to the optimisation of coagulation; choice of coagulant, it’s dose, the pH level, mixing arrangements, chemical addition, along with careful control and monitoring of downstream filtration and adsorption processes (Jacangelo *et al.*, 1995; ST design manual, 2006).

Enhanced coagulation, defined by Crozes *et al.* (1995) as ‘the addition of excess coagulants and adjustment of pH for improved removal of NOM’, is a process that has been shown to have a significant effect on the reduction of precursor material (Crozes *et al.,* 1995; Hooper *et al.,* 1996; White *et al*., 1997; Volk *et al.*, 2000; Garcia, 2005; van Leeuwen *et al*., 2005). Coagulation efficiency is greatly improved when pH has been lowered, with improved charge, making molecules more hydrophobic and absorbable (Randtke, 1988; Hooper *et al.*, 1996; van Leeuwen *et al*., 2005). Tryby *et al.* (1993) achieved a standard 34 % removal of TOC across a range of tests under different conditions. Without acid addition, 120 mg/l alum was required to achieve optimum TOC removal at pH 5.9. With acid addition, only 30 mg/l was required to achieve optimum TOC removal at pH 6.7 (*e.g.* 75 % less coagulant when the pH was reduced).

Although effective, enhanced coagulation is prohibitively expensive due to costs of acid dosing, extra coagulant and increased sludge production. NOM characteristics and alkalinity also affect the success / feasibility of this process. The hydrophobic / hydrophilic distribution of TOC plays an important role, since hydrophobic organic carbon is more susceptible to coagulation than hydrophilic organic carbon (Singer & Harrington, 1993; Nikolaou, 1999; Singer & Liang, 2004).

Granular activated carbon (GAC) is widely used in surface water treatment for the removal of trace concentrations of pesticides from drinking water and offers many side benefits, including the removal of taste and odour causing compounds, and THM precursor compounds. Average organic removal by GAC at Melbourne and Trimpley WTWs were quoted by Hua (1999) to be 19 % and 26 % respectively. These levels are slightly lower than those reported by Shurrock *et al.* (1999), who quoted removal rates at an average WTW to be between a maximum of 56% and an average of 39%. The efficiency of GAC depends on the temperature and nature of the substances in the water passing through the bed. Due to the accumulation of filtered material in the bed, the GAC will need to be periodically 'regenerated', a process which involves the removal of the polluting adsorbate and simultaneous re-establishment of the carbon’s adsorptive capacity. The most common method of doing this is thermal regeneration, where the spent carbon is heated in an inert atmosphere (to stop it from burning) at temperatures of around 800°C.

Courtis (2003) looked at the influence of GAC age (0.5 – 142 days) on chlorine demand, organics removal and THM formation. GAC age refers to time since first contact with water. The following observations were made. Typically, TOC removal was approximately 30%, although new GAC was found to remove up to 66 %. THM formation potential (THMFP) removal could be as high as 80% with new GAC, but in general was found to typically remove only 25%. Finally, after GAC has aged by 20 days it no longer caused a reduction in THM, with GAC at 140 days resulting in an increase in THM of 10 μg/l. Roberts (2004) showed GAC approximately 18 months old removed between 5 and 15 % of TOC, whereas 3 month old GAC removed between 40 and 50 % of TOC.

2.12.3 Removal of DBPs after formation

Each species of halogenated DBPs has different physical, chemical and biological properties. This means that employing a single treatment process that can remove them all is not possible. After DBPs have formed, they may be removed by physical, chemical, or biological methods. Such methods include air stripping, activated carbon and membrane processes (Clark & Adams, 1993; Nikolaou *et al*., 1999; WHO, 2005).

- *Air stripping or aeration* involves methods including the use of packed column air stripping towers, or the passing of large amounts of compressed air through the water, with the aim of allowing the contaminants to volatize in the air stream. Significant removals of THM have been observed by several researchers (Umphres *et al*., 1983; Bilello & Singley, 1986; Premazzi *et al*., 1997). In a pilot-scale plant with an air-water ratio of 38:1, a water loading rate of 21 mm/s, and a bed packing depth of 2.4 m, Umphres *et al*. (1983) observed a 78 %, 74%, 59 % and 45 % reduction of inlet concentrations of approximately 100 µg/l of chloroform, bromodichloromethane, chlorodibromomethane, and bromoform, respectively. The main drawbacks of this method include prohibitively high costs, non-definite removal, air contamination and residual disinfectant removal (Premazzi *et al*., 1997; Nikolaou *et al*., 1999).

- *GAC* has been shown to be effective at removing a wide range of organic compounds including both THM precursors and THMs after their formation. A powdered activated carbon (PAC) dose of 300 mg/l was found to be sufficient to reduce a chloroform concentration of 10 µg/l to less than 1 µg/l by Jacangelo *et al*. (1989). However, in fixed GAC beds, regular maintenance is necessary and microbiological contamination may take place (Premazzi *et al*., 1997). Moreover, GAC is rapidly degraded by chlorine and the addition of a disinfectant to the GAC bed can result in a specific reaction in which previously sorbed compounds leach into the treated water (Kim & Kang, 2008).

- *Membrane techniques* are gaining importance in the treatment of water sources for drinking water due to more stringent water standards, a decrease in adequate water resources, an emphasis on water reuse, and a decrease in the relative costs due to technological advancements (Uyak *et al*., 2008). Reverse osmosis has been demonstrated to remove between 85-90 % of all organic compounds (Premazzi *et al*., 1997). Nanofiltration has been successfully demonstrated to remove THMs from water, with increased removal on account of increasing molecular weight of THM species (Kimura *et al*., 2003; Uyak *et al*., 2008). The success of all membrane techniques is dependant on the compounds' physical and chemical properties (*e.g.* molecular size, solubility, diffusivity, polarity, hydrophobicity and charge), membrane properties (*e.g.* permeability, pore-size, hydrophobicity, and charge) and membrane operating conditions (*e.g.* flux, trans-membrane pressure and recovery) (Hass, 1999; Van der Bruggen *et al*., 1999; Kimura *et al*. 2003; Uyak *et al*. 2008).

2.13 Alternative disinfectants

The increasing challenges of removing or inactivating some of the most resistant pathogens (like Giardia and Crytosporidium), while minimizing disinfection by-products, have led to the use of alternative disinfectants gaining popularity. Disinfectants such as ozone, ultraviolet, chloramines, chlorine dioxide, and potassium permanganate provide viable alternatives to chlorine. However, as Appendix A demonstrates, each of these alternative disinfectants has their own advantages and disadvantages, in terms of their disinfectant abilities, residual effect, cost and ease of use. Also, in comparison to chlorine, which has been much more widely studied, there is little information about the DBPs that these alternative disinfectants produce. Thus, it is not known if the DBPs from alternative disinfectants are safer or more hazardous than those formed by chlorine (Richardson *et al*., 2000).

2.14 Linking the knowledge gap to the objectives of thesis

The preceding sections have highlighted a number of areas of uncertainty requiring further research. These are, in relation to the study objectives set out in chapter 1;

(i.) To undertake a detailed analysis and cross comparison of THM formation and chlorine decay in six water supply systems, relating the differences to WTW operational and source water characteristics, supply procedures, and temporal and spatial variation in each of the foregoing, in order to try and understand critical factors in each of the six systems: There is increasing concern over disinfection by-products due to more stringent regulatory standards and recent developments in epidemiological techniques. The large proportion of the work undertaken regarding the formation of THMs has concentrated on laboratory-based studies looking at conditions not typically found in present day water supply systems. Additionally, much of the research investigating THM formation through the WTW has been based in countries with characteristically different waters and treatment techniques to those found in the UK. There is a need, therefore, to understand how THMs are formed in-situ through both the WTW and the distribution system under ambient conditions, to allow for an accurate portrayal of system response under typical operational conditions across a range of UK based source waters.

(ii.) To investigate the influence of water quality parameters, initial chlorine concentration, temperature, contact time, water treatment unit and supply processes on chlorine decay, in order to develop empirically based models to relate functional dependencies: The majority of previous studies have focused on chlorine decay within treated waters sampled from either WTW final waters or in distribution systems. To further knowledge of chlorine decay it is important to have the knowledge of how and where the reactivity of the water changes from raw to final water through the WTW. This involves investigating how the water quality changes and the impact on chlorine decay of each water treatment process. There is also a need to relate this variation to analytically undemanding parameters that can be routinely monitored under operational circumstances.

Most existing chlorine decay models have been based on studies where pre-chlorination was still practised. As there is now broad consensus that pre-chlorination is unjustified due to problems with excessive DBP formation, there is a need for a more rigorous assessment of chlorine decay under such conditions. Specific emphasis can now be placed on the contact tank as this is now the location at most WTWs where first chlorination takes place. There has also been considerable debate over which kinetic model is best suited to represent chlorine decay and whether the complexities of using higher order and more complicated models are justified. It would therefore be of theoretical significance to clarify these issues to produce appropriate equations and coefficients, which are adaptable to a range of operational scenarios.

(iii.) To investigate THM formation in relation to key water quality parameters, initial chlorine concentration, temperature, contact time and water treatment unit and supply processes, and consequently to determine appropriate THM formation models: None of the THM prediction models developed to date could be classed as truly predictive, due primarily to the complexity of THM reactions and the intricate mixture of compounds forming a water’s chemical matrix. Thorough experimental work, and empirically based models on such experiments, are currently still the best way to understand the THM issue at WTWs and in distribution. Most existing THM formation models are empirical and include a number of constants having no physical meanings, which must be determined by experiments. In order to demonstrate the reliability and applicability of these models, experiments must be carried out which not only need a substantial amount of data but also are very expensive. Therefore, it is desirable to develop simple theoretical or semi-theoretical models with only a few parameters which can determined by simple experiments. Work done by Clark (1998), Clark and Sivaganesan (1998) and Hua (1999) showed that there is strong link between the TTHM and consumed chlorine. It is therefore important to investigate the relationship between the chlorine consumed and the TTHM formed for a range of chlorination conditions and water types to demonstrate its reliability. The underlying influence of the variation of C_0, TOC, bromide, temperature and contact time on this relationship also requires more investigation to give a rigorous assessment of its merit.

As the majority of previous studies have focussed on treated and distribution system waters, there is also a need to investigate the influence of each unit process on the THM formation in conjunction with the chlorine decay and compare this with water quality and operational conditions across a range of UK based source waters. This will allow for an improved understanding of treatment optimisation with specific emphasis on reducing THM formation.

(iv.) To consolidate the analysis into a cost-effective, spreadsheet model that can be practically applied in operational circumstances, enabling the user to enter prevailing water quality and WTW operational characteristics to predict chlorine use and THM formation from source water to customer tap: Although there has been a vast amount of research concerning the formation of THM and chlorine consumption, there is still the need to provide a robust, yet straightforward approach to modelling both parameters, which can be utilised by operational staff in the field. Previous models intending to do this have relied on large expensive datasets or extensive calibration which is time consuming and operationally inhibitive. Thus a simple and cost effective, yet efficient model will aid as a useful management tool, allowing for economical and efficient management decisions.

The majority of previous studies of THMs and chlorine have been based on data obtained from either field-based or laboratory scaled studies. Whereas field-based studies have the advantage of ambient operational conditions, laboratory based studies offer the advantage of offering controlled conditions, where parameters can be isolated for investigation. There is a need for the advantages of both methods to be utilised in a pooled analysis. A cross analysis between different waters under similar laboratory controlled conditions will allow for a more comprehensive understanding of source water characteristics, operational conditions etc.

(v.) To apply and critically evaluate the proposed model for one of the supply systems studied, thus identifying mitigation strategies for the management of THMs: Finding a balance between disinfection efficiency and the control of DBPs in potable water supplies is becoming increasingly precarious for water companies, as increasingly more stringent regulatory standards are enforced. As the factors affecting DBP formation are based in such minute proportions, the relationships between water quality parameters and THM formation will be system specific. Thus management decisions for one system will not be directly applicable to other systems with different water quality and operational characteristics. However, the broad principles to help with the management of a system and also the basic structure of a model relating to THM formation would be useful as an initial assessment.

Reference	**k_b** (l/hr)	**k_b + k_w** (l/hr)	**Measurement Method**	**Details**
AWWARF 1996	0.005	0.18	*In situ* test	Free, 250mm diameter, CI, C_o =0.3mg/l
		0.13		Free, 250mm diameter, CI, C_o =0.6mg/l
		0.11		Free, 250mm diameter, CI, C_o =1.0mg/l
		0.06		Free, 250mm diameter, CI, C_o =5.2mg/l
	0.008 – 0.030	0.009	Laboratory Rig	Free, 150mm diameter, HDPE, 18^{o}C
		0.024		Free, 150mm diameter, PVC, 18^{o}C
		0.021		Free, 100mm diameter, PVC, 18^{o}C
		0.016		Free, 150mm, Glass Re. polyester, 18^{o}C
		0.042		Free,100mm diameter, Polyprop.,18^{o}C
Beatty *et al.*, 1996		0.06 – 0.15	*In situ* test	No details known
		0.10 – 0.70		No details known
		0.00 – 1.40		No details known
Brammer and Tansley 1993		0.088	*In situ* test	Free, 152mm diameter
		0.039		Free, 356mm diameter
		0.031		Free, 406mm diameter
		0.022		Free, 600mm diameter
Burgees *et al.*, 1996		0.523 – 0.640	*In situ* test	Total, Unfiltered, 1350mm diameter
		0.126 – 0.126		Total, Unfiltered, 1350mm diameter
		0.045 – 0.073		Total, Unfiltered, 1050mm diameter
		0.290 – 0.315		Total, Unfiltered, 900mm diameter

		0.134 – 0.136		Total, Unfiltered, 600mm diameter
		0.095 – 0.178		Total, Unfiltered, 500mm diameter
		0.194 – 0.236		Total, Unfiltered, 450mm diameter
		0.219 – 0.330		Total, Unfiltered, 375mm diameter
		0.082		Total, Unfiltered, 300mm diameter
		0.521		Total, Unfiltered, 200mm diameter
		0.540		Total, Unfiltered, 150mm diameter
		0.562		Total, Unfiltered, 100mm diameter
		0.101		Total, Filtered, 375mm diameter
		0.096		Total, Filtered, 300mm diameter
		0.111		Total, Filtered, 250mm diameter
		0.0775		Total, Filtered, 200mm diameter
		0.121		Total, Filtered, 150mm diameter
		0.471		Total, Filtered, 100mm diameter
Chambers *et al.*, 1995	0.03	0.22 – 0.39	Calibration of Decay constants in Network models	Free, CI and Asbestos cement, 11^{o}C
	0.04	0.10 – 0.22		Total, CI and Asbestos cement, 11^{o}C
	0.21	0.25 – 0.33		Free, CI, 8^{o}C
	0.12	0.13 – 0.28		Total, CI, 8^{o}C
Clark *et al.*, 1993	0.02	0.03 – 1.06		Free
Rodriguez *et al.*, 1997		0.03 – 0.06	*In situ* test	Free, DICL
Sharp *et al.*, 1991		0.324	*In situ* test	Free, 150mm CI
		0.240		Free, 300mm CI
		0.204		Free, 300mm PVC
Woodward		0.051 –	Laboratory	Total, MDPE, 0.07 – 0.90 l/s flow rate

et al., 1996		0.173	Rig	
Zhang *et al.*, 1992	0.114	0.126 – 0.138	*In situ* test	Free, 500mm Asbestos, 31°C, TOC 1.1mg/l
	0.072	0.054		Free, 700/800mm Steel, 30°C, TOC 1.0mg/l
	0.072	0.066		Free, 500mm Steel, 28°C, TOC 1.2mg/l

Table 2.1; Decay constants (specifically related to wall decay) as reported in various studies (*as cited* in Hallam, 1999)

Group	**Prominent examples**
Trihalomethanes (THMs)	Chloroform
	Bromoform
	Bromodichloromethane
	Chlorodibromomethane
Haloacetic acids (HAA)	Monobromoacetic acid
	Bibromoacetic acid
	Tribromoacetoc acid
	Bromochloroacetic acid
	Bromodichloroacetic acid
	Dibromochloroacetic acid
	Trichloroacetic acid
	Dichloroacetic acid
Haloacetic Nitriles (HANS)	Dichloroacetonitrile
	Trichloroacetonitrile
	Dibromoacetonitrile
	Tribromoacetonitrile
	Bromochloroacenitrile

Cyanogen halides	Cyanogen chloride
	Cyanogen bromide
MX (3-chloro-4-dichloromethyl-5-hydroxy-2-5H-furanone)	Monochloroacetic acid
	Dichloroacetic acid

Table 2.2; Major DBP classes and prominent / common examples found in drinking water (*as cited* in Singer, 1994)

Drinking water contaminant	**Cancer classification (see Table 2.4 for classification)**
Chloroform	B2
Bromodichloromethane	B2
Chlorodibromomethane	C
Bromoform	B2
Chlorate	-
Chlorite	D
Bromate	B2
Hypochlorous acid	-
Hypochlorite	-

Table 2.3; Statutes of health information for chlorine disinfectants and DBPs (*as cited* in USEPA guidance document EPA-815-R-99-014 (1999)).

Group	**Description of scheme of classification**
Group **A**: human carcinogen	Sufficient evidence in epidemiological studies to support casual association between exposure and cancer.
Group **B**: probable human carcinogen	Limited evidence in epidemiological studies (Group B1) and / or sufficient evidence from animal studies (Group B2)
Group **C**: possible human carcinogen	Limited evidence from animal studies and inadequate or no data in humans.

Group **D**: not classifiable	Inadequate or no human and animal evidence of carcinogenicity.
Group **E**: no evidence of carcinogenicity for humans	No evidence of carcinogenicity in at least two adequate animal tests in different species or in adequate epidemiological and animal studies.

Table 2.4; The scheme for categorizing chemicals according to their carcinogenic potential (as cited in USEPA guidance document EPA-815-R-99-014 (1999)).

THM species	**Molecular weight**
Chloroform ($CHCl_3$)	119.5
Chlorodibromomethane ($CHClBr_2$)	208.5
Bromodichloromethane ($CH Br Cl_2$)	163.8
Bromoform ($CHBr_3$)	252.7

Table 2.5; Molecular weights of the four main THM species.

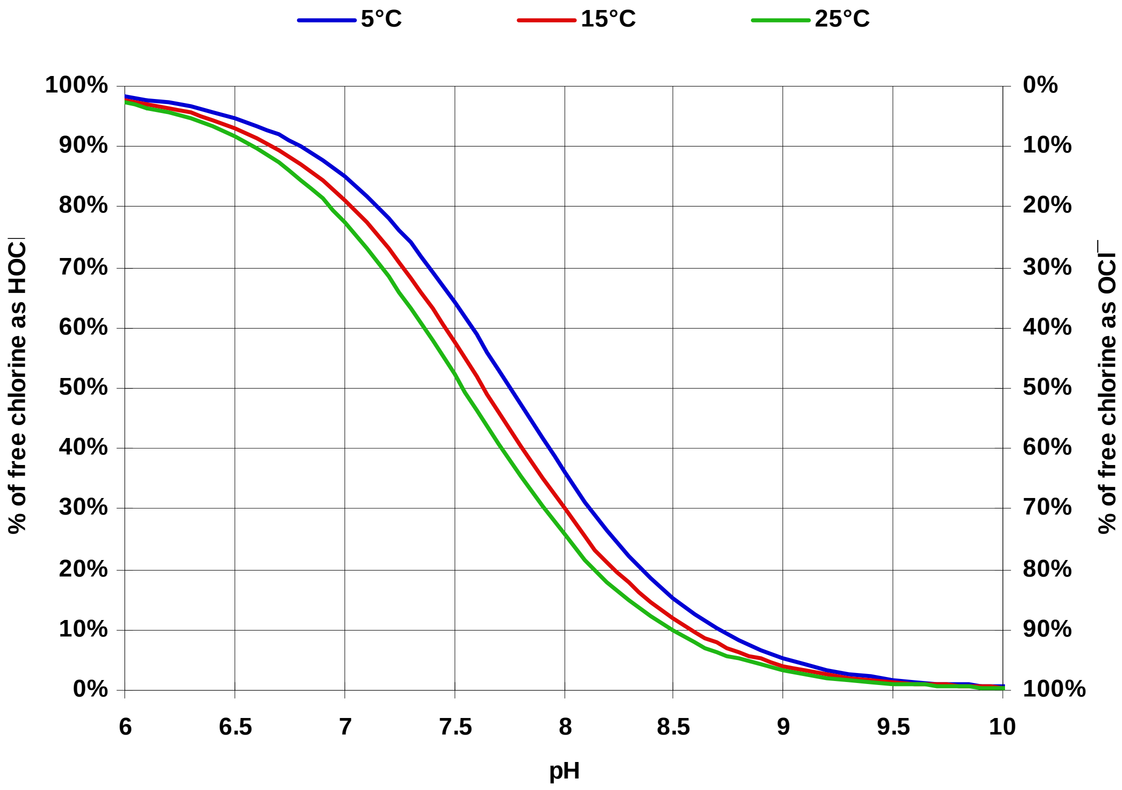


Figure 2.1; Distribution of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) in water at different pH values and temperatures.

Chapter 3 Materials and methods

3.1 Terminology and measurement techniques

This section details the terminology and measurement techniques for all parameters used throughout this study. Methods for laboratory tests and field surveys are described and assessments of the relative errors of measurement are discussed. Severn Trent Laboratories (STL) provided the methodology for all analyses conducted by the Company.

3.1.1 Free chlorine

The term ‘free available chlorine’ is used to refer to the sum of the concentrations of molecular chlorine (Cl_2), hypochlorous acid (HOCl), and hypochlorite ion (OCl^-). At all sites surveyed in the study, STW use and monitor free chlorine as the predominant form of disinfectant.

Chlorine measurement techniques are generally divided into three groups; colorimetric, titration and amperometric methods. In this study, all spot and UoB laboratory samples were measured by the DPD (di-methylphenylene diamine) colorimetric method using Hach pocket colorimeters (Camlab, Cambridge) (Figure 3.1). STW uses the same equipment for regulatory sampling and calibration of on-line chlorine monitors. A comparison of the colorimetric and titration methods has been made for several samples and showed good agreements (R^2 ~ 0.990, RMS error ~ 0.031 mg/l) (Powell, 1998; Hua, 2000).

The following sampling procedure was used for all free chlorine measurements, as described by Powell (1998) as the 'single Hach procedure';

1. Wash two sample cells thoroughly with the sample water to avoid contamination of samples.

2. Fill two sample cells with sample water to the 10 ml mark.

3. Wipe the cells dry, removing any fingerprints and dirt with a soft paper towel. Check cells are not scratched.

4. Insert one cell into the pocket Hach colorimeter and set to zero. This eliminates any interference with the natural colour within the sample water. Check battery power as low power produces erratic readings. All readings should be conducted in the shade to avoid effects from changes in the surrounding light intensity.

5. Ensure that the zero reading is obtained from the second cell and reset as required until a zero reading is obtained for both sample cells.

6. Add a sachet of N, N-diethyl-p-phenylendiamine (DPD No. 1) powder to one of the sample cells and shake for approximately 20 seconds or until no DPD reagent remains in suspension. Leave for a further 10 seconds to ensure all reactions between the reagent and the free chlorine are completed.

7. Place the prepared sample into the Hach meter and repeatedly take readings until three consecutive similar readings are obtained. If stable readings are not obtained within two-minutes of adding the reagent, the sample should be replaced, since the DPD reagent will slowly react with combined chlorine to produce a coloured complex.

8. The zero value should then be rechecked using the other sample. If it is found have drifted the reading should be ignored and the process repeated.

All samples during the survey were taken in duplicate and crossed-checked on two pocket chlorine colorimeters. Therefore, an average of four concentration values were obtained, a process termed the ‘double Hach procedure’ within this thesis. This was done to statistically reduce any measurement errors that may occur and enabled any abnormal behaviour in one of the pocket Hach colorimeters to be identified.

All Hach meters were checked on a regular basis against a set of coloured gel standards supplied by the manufacturer and were always found to be within ± 0.02 mg/l with a repeatability of 0.01 mg/l. Powell (1998) and Hallam (1999) undertook a comprehensive review of the errors associated with the measurement technique. The calculated standard error for the double Hach procedure was only ± 0.01 mg/l (Powell, 1998).

In addition to spot and laboratory chlorine samples, readings were taken from permanent monitoring installations within the WTWs and distribution systems (which were operated and maintained by STW personnel). The monitors use an amperometric method to measure the chlorine residual. The water is buffered to reduce the pH and an electrode selectively attracts hydrogen ions, which then produce an electric current that is proportional to the concentration of HOCl in the water. Triple validation (involving the use of three monitors in parallel) is employed at most of the sites to improve confidence in results.

3.1.2 Total chlorine

All samples used to determine the concentration of total chlorine (the sum of free and combined chlorine species) were determined using the pocket colorimeters in the same way as performed for free chlorine. A different reagent (DPD No. 3) is added to the sample water, which reacts with total chlorine. All glassware for these measurements was kept separate from those used for free chlorine measurements. The manufacturer’s stated error was ±0.02mg/l with a repeatability of 0.01mg/l

3.1.3 Trihalomethane (THM)

In order to investigate THM formation within both the WTW and distribution system a total of 278 spot and laboratory THM measurements were taken by the author and submitted to STL for measurement.

For this study, the THM analyses measured the concentrations of chloroform, bromodichloromethane, chlorodibromomethane and bromoform. The individual concentrations of these species were then summed together on a mass basis to obtain the total trihalomethane concentration (TTHM). THMs can be determined by a number of different analytical techniques, including purge-and-trap, liquid-liquid extraction, and direct aqueous injection in combination with a chromatographic system (WHO, 2005).

For THM samples taken during the field surveys and in laboratory work the following procedure was applied;

1. Sample water was poured into a 40 ml amber coloured glass vial, ensuring no remaining air was present when sealed. The vials contained sodium thiosulphate ($Na_2S_2O_3$) at a concentration of 0.003% when the bottle was filled with sample water. The use of sodium thiosulphate eliminated any further reactions involving residual free chlorine to continue formation of THM once the sample had been taken.

2. The samples were then immediately refrigerated prior to being taken to the STL courier point at Tile Hill, Coventry. If taken as part of field surveys, THM

samples were stored during transportation in controlled incubators prior to being transferred to STL.

The THM concentration at STL was determined using a headspace gas chromatography (GC) with electron capture detection. The basic underlying principle of this method, as described by Manahan (1994) and Nikolaou *et al*. (2002), is as follows. A carrier gas transports a mixture of volatile materials through a column containing an adsorbent solid phase, or an absorbing liquid phase coated on a solid material. Each volatile component is then partitioned between the carrier gas and the solid or the liquid. The length of time required for the volatile component to move within the column is proportional to the degree to which it is retained by the non-gaseous state. Different components will emerge from the column at different times and are measured by a detector in terms of their quantity and time they emerge.

The equipment used by STL for this procedure is a HP6890 gas chromatograph fitted with electron capture detector and a Perkin Elmer turbomatrix 110 autosampler / headspace unit. The quoted accuracy for the four main THMs were; chloroform ~ ± 9.3%; bromodichloromethane ~ ± 9.0%; chlorodibromomethane ~ ± 11.9%; bromoform ~ ± 11.9%.

3.1.4 Temperature

Temperature governs the rate of most chemical reactions that will occur in natural water systems and will also affect the nature and quantity of biological species present. All spot and laboratory temperature readings were taken using a standard mercury thermometer, graduated to 0.5 °C.

3.1.5 pH

The quantity pH is intended to be a measure of the activity of hydrogen ions in solution (IUPAC, 2002). It is a measure of the acidity or basicity of a solution, based on a logarithmic scale from 0 to 14 called the “Pondus Hydogeni”. The pH of most natural waters typically lies in the range of 4.5 to 8.5, varying primarily due to the nature of the source environment (*e.g.* groundwater is usually slightly alkaline due to the reactions of water with dissolved carbonate ions). In water treatment, the measurement of pH is one of the most important and frequently tested parameters since many of the treatment processes involved are pH dependant. All pH measurements taken in this study were undertaken in the UoB Public Health Laboratory with a 320 pH meter manufactured by Mettler-Toledo Ltd. The meter was calibrated and checked regularly against standard buffer solutions. The manufacturer’s quoted (relative) accuracy is ± 0.01 pH.

3.1.6 Bromide

The diatomic element, bromine (Br_2), is generally not present in the natural environment. In natural water it is always present as the bromide ion (Br^-).

For bromide samples taken during the field surveys, and in laboratory work, the same procedure used for the collection and storage of THM described in section 3.1.4 was applied with the only difference being 250 ml amber glass bottles were used instead of the 40 ml vials used for THM.

The bromide concentration at STL was determined using direct injection ion chromatography, using an anion exchange column with a bicarbonate eluent and suppressed conductivity detection. The equipment used was a Dionex DX600 and Dionex AS9-HC separator column. The quoted accuracy for the bromide measurements was ± 3.4 %.

3.1.7 TOC

Natural organic matter (NOM) is ubiquitous in surface and ground water sources in many varieties. Nearly 1000 organic contaminants have been identified in drinking water, present at nanogram to microgram concentrations (Ram, 1986). Because NOM characteristics are widely varied, both chemically and physically, no single, cost effective analytical technique is available to characterize NOM. As a result, surrogate parameters such as organic carbon content must be used to describe generalized NOM characteristics. TOC is one such surrogate, defined as “the quantity of carbon atoms which are covalent bonded in organic molecules”.

To determine the TOC concentration in a sample water, the organic molecules must be broken down to single carbon units and converted to a single molecular form which can be measured quantitatively. This is typically achieved using heat, oxygen, ultraviolet irradiation, chemical oxidants, or combinations of oxidants that convert organic carbon to carbon dioxide. Subsequently, the carbon dioxide may be measured directly, by a non-dispersive infrared analyser; it may be reduced to methane and measured with a flame ionisation detector; or may be titrated chemically. Results are generally reported in mg/l and are typically rounded to two significant figures.

Since the measurement of organic carbon is essentially based on the analysis of the carbon dioxide produced as a result of oxidation of that organic carbon, any carbon dioxide or other sources of carbon dioxide present, will give rise to a positive interference and erroneous results. Dissolved carbon dioxide and inorganic carbonates and bicarbonates are removed prior to measurement by techniques such as the addition of acid. In addition to this, the presence of oxidising agents (*e.g.* hydrogen peroxide, hypochlorous acid, etc.) may also give rise to an increased TOC response if present in sufficient quantities. This is probably due to the oxidation of traces of residual carbonaceous material in these compounds.

In this study a total of 129 TOC samples were taken through the six WTWs and their respective distribution systems. All samples were collected in clean, transparent, half or one litre plastic bottles supplied and prepared by STL. Samples were refrigerated until delivery to STL laboratories.

At STL, TOC was measured using a PPM LabTOC analyser with auto-sampler, printer and computer system. The methodology is as follows. The sample is mixed with acidified persulphate solution and any inorganic carbon present in the sample is purged off as carbon dioxide. An aliquot of the stabilised sample is then passed into the reaction vessel where irradiation with UV in the presence of persulphate causes all the carbon to convert to carbon dioxide. This carbon dioxide is swept by an inert carrier gas (nitrogen) to an infra-red detector where the concentration of the carbon dioxide present is determined. The stated accuracy of the method is ± 7.4 %.

3.1.8 Colour

Colour comes primarily from natural organics in the water (*e.g.* tannins, humics etc.) derived from decayed plant matter. When light is transmitted through a depth of several metres of pure water, the water appears light blue in colour. With an increase in organic content, however, the colour of the water can change from blue to green and through a variety of shades down to brown. From an analytical view point, colour can be described as either ‘true’ or ‘apparent’. True colour is that colour due to dissolved matter in the liquid only, whereas apparent colour is that colour seen in the presence of suspended matter. Therefore, the difference between the two measurements is that true colour samples are passed through a 0.45µm membrane to remove the suspended matter prior to measurement.

At STL, measurement of colour is achieved using a Spectrophotometer (at a wavelength of 400 nm, with a path length of 40 nm) and auto-sampler. The quoted accuracy of determination is ± 7.2 %, with units usually given in Hazens.

3.1.9 UV_{254} absorbance

One of the most commonly applied surrogates in drinking water research has been the measurement of a water’s ability to absorb ultraviolet light. The usual wavelength used for measuring UV absorbance is 253.7 nm (approximated to 254 nm), which corresponds to the strongest line of the emission spectrum of a low-pressure mercury lamp.

UV_{254} absorbance indicates the concentration of organic molecules with aromatic groupings or extended conjugation (Edzwald, 1985). The principle behind this method is that UV-absorbing constituents will absorb UV light in proportion to their concentration.

This study used results collected from routine measurements by STW personnel and samples conducted at STL in a non-accredited test carried out specifically for STW. The method for determination is fundamentally the same as for colour but at a different wavelength (253.7 nm).

3.1.10 Turbidity

Turbidity is the cloudiness or haziness of a water caused by individual suspended particles, ranging in size from colloidal to coarse dispersions. The measurable proportion of the suspended matter in water, which interferes with light passing through it, is referred to as turbidity, and is usually measured in Formazin Turbidity Units (F.T.U) or Nephelometric Turbidity Units (N.T.U).

Turbidity is measured at each treatment process stage, at regular intervals during the day, at each of the WTWs investigated. Data are entered onto the Severn Trent databases by WTW operational staff. All online measurements are triple validated (Figure 3.2) and their accuracy checked by STL by a 2100-N Turbidimeter (Camlab, Cambridge).

3.1.11 Determination of travel times

When considering the formation of THMs and the decay of chlorine in distribution systems, an understanding of the relevant hydraulic information is essential in order to gather realistic travel time information. Flow meters within a system are often limited as they are expensive to install and their accuracy is often difficult to assess. Pressure monitoring provides an alternative, however this is only accurate where pressure gradients are high and pipe characteristics such as diameters and friction factors are known (which in practice is difficult to ascertain to a high degree of accuracy). Tracer studies offer the flexibility to determine travel time to virtually any point in the system. However, they are often only practical when a suitable, operationally flexible, parameter (such as fluoride) can be temporally turned off and then back on. Alternatively, tracer studies may be performed through injecting a readily identifiable substance (such as lithium) into the system. This again has drawbacks; including injecting a potentially hazardous chemical, albeit at low concentrations, into the water supply which is deemed undesirable. It also requires extensive planning, safety precautions and specialized personnel, all of which come at an economical cost.

For the modelling aspect of this work the travel times have been estimated via the use of data obtained from STW all mains models of the relevant distribution systems. These models have been formed through a combination of in-house hydraulic modelling simulations and tracer studies using fluoride (where fluoridation is practiced in the system). As the data is based on average flow conditions the use of the model is restricted due to the variable diurnal and seasonal factors influencing flow conditions not being accounted for. However, for the ultimate purpose of modelling THM formation, the travel time information is deemed acceptable as the most useful and operationally practical data to use. Further clarification regarding the influence of such diurnal and seasonal factors could be incorporated into the model to enable the effects of changes in flow to be assessed.

3.2 Determination of chlorine decay

3.2.1 Bulk chlorine decay

The determination of bulk chlorine decay was carried out using a similar procedure to that reported by Powell (1998) and Courtis (2003). The full sampling procedure is as follows (for samples with an ambient chlorine concentration);

1. All glassware was treated to ensure that any chlorine demand exerted by the glass had been satisfied in accordance with methods detailed by the Department of the Environment (1981):

    - Freshly cleaned glassware was filled with distilled water, which had been dosed to 10 mg/l free chlorine using concentrated sodium hypochlorite.
    - The glassware was left to stand for 24 hours before being emptied and rinsed thoroughly three times with distilled water and left to dry.

2. A 2.5 litre Winchester bottle was filled with sample water.

3. The water was then thoroughly mixed using a magnetic stirrer to ensure homogeneity for approximately 1 minute.

4. The chlorine concentration within the Winchester bottle was then determined using the double Hach procedure (as detailed in section 3.1.1). The time and concentration were recorded, as the start time and initial chlorine concentration.

5. The sample water was then decanted into eight 250 ml glass amber bottles that were sealed with glass stoppers, ensuring no air remained inside.

6. All samples were stored in an incubator set to either ambient (or control) temperature of the water sample under investigation. Samples taken in the field were stored in a refrigerated box prior to being incubated at laboratories at the UoB.

7. The free and total chlorine concentrations were determined at pre-determined time intervals according to test conditions.

8. The results were then entered onto a spreadsheet and the decay constant calculated for a first order using the Excel linear regression tool and the following equation:

$$\ln (C/C_0) = -K_B.t \tag{3.1}$$

Where: C = Chlorine concentration at time, t (mg/l)

C_0 = Initial chlorine concentration at time, 0 (mg/l)

t = Time (hours)

K_B = Bulk chlorine decay constant (l/hr)

Where the sample water contained no ambient chlorine, at step 2, sodium hypochlorite solution was added to the sample water to make up the pre-defined free chlorine concentration at a known volume. This concentration and time were then taken as the initial chlorine concentration and start time. After the water was thoroughly mixed using a magnetic stirrer to ensure homogeneity for a period of 1 minute, the sample water was decanted into amber glass bottles (as in step 5) and the tests conducted as in the remaining steps. Full details as to the number and type of bulk decay tests undertaken on the sampling days are provided in section 3.2.3.

Tests on the accuracy of the bulk decay test methodology were analysed by Powell (1998). A series of tests on distilled water showed a decay constant of 0.005 l/hr or less. Any decay would be due to limitations in the test methodology as distilled water should have zero decay as it contains nothing for the chlorine to react with. This was deemed acceptable as it was less than 10 % of the average bulk decay constant recorded during the whole survey.

3.2.2 Wall chlorine decay

The following provides a method to describe the decay rate between two points A and B in a distribution system, as described by Powell (1998) and Hallam (1999);

1. The bulk decay rate is measured at point A as described in section 3.2.1.

2. The average upstream or initial chlorine concentration, C_0, over approximately 20 minutes is taken for a slug of water at point A.

3. The travel time, t, is calculated from point A to point B for that slug of water. This is obtained either from flow meter records or from tracer studies.

4. The downstream of final chlorine concentration, C, was measured as the slug of water arriving at point B. An average over approximately 20 minutes was taken to ensure that the correct slug of water was measured. If a tracer study was used to calculate travel time then the period immediately prior to the trace being observed was used as the final chlorine concentration.

5. The overall and wall first order decay rate constants were then calculated by rearranging equations 3.1 and 2.19:

$$K = 1/t \,.\, \ln (C/C_0) \tag{3.2}$$

$$K_W = K - K_B \tag{3.3}$$

3.2.3 Description of bulk decay tests undertaken

On each of the sampling days at the six WTWs during the summer of 2007 the following tests were carried out:

(a) Contact tank simulation (ambient conditions with THM / Br samples)

Objectives:

- To observe chlorine and bromide decay and THM formation in post-GAC water at ambient conditions observed on the day of sampling, in order to simulate the contact tank operation, thus aiding modelling purposes.

Methodology:

- Water was collected from the post-GAC sampling points, transported and stored at the ambient temperature on the day of sampling.
- Water was dosed to an initial chlorine concentration (the same as that observed at the pre-contact tank sampling point on the day of sampling) and tests carried out following the methodology described in section 3.2.1.
- Free and total chlorine samples were taken at 5, 10, 15, 30, 45, 60, 90, 120, and 240 minutes in accordance with the methodology outlined in section 3.1.1 and 3.1.2 respectively.
- THM and bromide samples were taken at 5, 15, 60, 120 and 240 minutes in accordance with methodology outlined in section 3.1.3 and 3.1.6, respectively.

(b) Contact tank variation (varying temperature, C_0, and sample water strength)

Objectives:

- To simulate chlorine decay across the contact tank, varying the initial chlorine (C_0), temperature and sample water strength (through dilution with distilled water), to allow for an understanding of the reactivity of the water under different conditions typically observed at the WTW.

- THM and bromide measurements taken at the end of each of the two-hour bulk decay tests to aid quantifying the relationships between chlorine consumed, THM formed and operational parameters.

Methodology;

- Water was collected from post-GAC sampling points and transported and stored at the relevant temperatures for the proceeding tests.
- Bulk decay tests were conducted over two-hour period, varying the initial free chlorine concentration (1.3 mg/l, 1.7 mg/l, and 2.1 mg/l), sample water dilution (1:0, 2:1, and 1:2 parts sample water to distilled water), and temperature (5 °C, 15 °C, 25 °C).
- When the variation of one parameter took place, the remaining two parameters remained constant at either 1.7 mg/l, 15 °C and 1:0 for the initial chlorine concentration, temperature and sample water dilution, respectively. Therefore, in total, seven bulk decay tests (one of which was pertinent to each of the three variations) were conducted on each of the sampling days.
- Free and total chlorine samples were taken at 5, 10, 15, 30, 45, 60, 90 and 120 minutes from start of test in accordance with the methodology outlined in section 3.1.1 and 3.1.2 respectively.
- Single THM and bromide samples were taken at 120 minutes, in accordance with methodology outlined in section 3.1.3 and 3.1.6, respectively. The initial THM concentration was assumed to be negligible and the initial bromide concentration taken to be the same as the post-GAC spot sample taken on day of sampling.

(c) Final water and distribution service reservoir (DSR) towards end of distribution system

Objectives;

- To observe chlorine and bromide decay and THM formation in the final waters at each of the WTWs under ambient conditions to allow for representation of water at the start of the distribution system and to contrast with data at the WTW.
- To observe chlorine decay and THM formation towards the end of each of the distribution systems at ambient conditions to allow for representation of water at the end of the distribution system and to contrast with data from preceding points in the distribution system and final water.

Methodology;

- Water was collected at the final water or DSR sampling point in a suitable container, ensuring water was thoroughly mixed to ensure a homogeneous chlorine concentration. The ambient chlorine concentration was then taken as the initial chlorine concentration and the water decanted into the appropriate bottles and the test proceeded according to the methodology outlined in section 3.2.1.
- Water was transported and stored under the ambient temperature conditions observed on the day of sampling for the duration of the test period.
- Bulk decay tests were conducted over 24 hours.

- Free and total chlorine measurements were taken at 15 and 30 minutes, 1, 2, 4, 6, 8, and 24 hours from start of test in accordance with the methodology outlined in section 3.1.1 and 3.1.2 respectively.
- For final water samples, THM and bromide samples were taken at 30 minutes, 2, 4, 8 and 24 hours, in accordance with methodology outlined in section 3.1.3 and 3.1.6 respectively, with initial THM concentration and the initial bromide concentration taken to be the same as the final water spot sample taken on the day of sampling.
- For DSR water samples, a single THM measurement was taken at the end of the 24-hour test period, in accordance with the methodology outlined in section 3.1.3.

(d) Raw water

Objectives:

- To observe chlorine decay and THM formation in the raw waters at each of the WTWs to allow for a representation of the potential reactivities of WTW source waters prior to any water treatment practices. All tests were conducted under the same test conditions as in (b) to allow for comparison with post-GAC water.

Methodology:

- Water was collected from the raw water sampling points, transported and stored at a temperature of 15°C.
- Water was dosed to an initial chlorine concentration of 1.7 mg/l (the same as the common test from (b)) and tests carried out following methodology described in section 3.2.1.

- Free and total chlorine samples were taken at 5, 10, 15, 30, 45, 60, 90, and 120 minutes in accordance with methodology outlined in section 3.1.1 and 3.1.2 respectively.
- Single THM and bromide samples were taken at 120 minutes, in accordance with methodology outlined in section 3.1.3 and 3.1.6 respectively. The initial THM concentration was assumed to be negligible and the initial bromide concentration was taken to be the same as the raw water spot sample taken on the day of sampling.

(e) Additional tests carried out at Strensham WTW and distibution system

In addition to the work described above, further bulk decay tests (both numerically and spatially) were conducted through Strensham WTW and distribution system to allow for a more accurate spatial and temporal picture of THM formation and chlorine decay. Additional bulk decay tests, conducted under the same test conditions and methodology as the raw water tests (d), were carried out on water sampled from the post-clarifier and post-RGF sampling points. A further sampling point was also used in the Shipston distribution system (Oversley Green BPS outlet), to conduct bulk decay tests under similar conditions and a methodology used in part (c).

3.3 Study sites

Severn Trent Water Ltd is one of the United Kingdom's largest water utilities, covering an area of about 8,000 square miles between the Humber and Severn estuaries. The company supplies approximately 2,000 Ml/d to a population in excess of 8 million people and also treats all the wastewater from the same population. The Company operates 17 major surface water abstraction water treatment works and around 180 groundwater abstraction sources. A significant feature of the supply system is its strategic treated water grid, which links 13 of the 17 major WTWs and contributes to the supply of water to approximately 75 % of STW customers (Figure 3.3).

The majority of experimental results have been gained from work undertaken on six water treatment works and associated stretches of their distribution systems. The following section provides a brief overview of each of the six WTWs; their current treatment practices, operational capacities and a description of the investigated distribution system. Each of the DSRs and booster pumping stations (BPS) studied were chosen as they received water solely (or if not feasible, as much as possible) from the relevant WTW under investigation. Typical source water characteristics are summarized in Table 3.1.

3.3.1 Strensham WTW and its distribution system

Strensham WTW supplies parts of the Worcestershire, South Warwickshire and Coventry systems. Water is abstracted directly from the River Severn (with no raw water storage), and is treated via a process train comprising screening, biological filters, coagulation / flocculation, clarification (HBCs), filtration, GAC, and disinfection (see Figure 3.4 for process flow sheet). Minimum and maximum flows through the works are 70 and 160 Ml/d respectively.

The DSRs and BPSs investigated in the Shipston leg of distribution are (in sequential order from Strensham final water); Oversley Green BPS, Bordon Hill DSR, Feldon BPS and Brailes

DSR, which feeds two subsequent legs; 1. Great Wolford BPS and Little Compton DSR; and 2. Tysoe DSR (Figure 3.5).

3.3.2 Melbourne WTW and its distribution system

Melbourne WTW is located near to the Derbyshire / Leicestershire border near Ashby-de-la-Zouche. Water is extracted from the River Dove (which rises in the southern Peak District) at Egginton, just before the confluence with the River Trent near Burton upon Trent, and then is stored in Staunton Harold and Foremark reservoirs (about 30 days) before treatment. The process flowsheet at the works comprises coagulation / flocculation, clarification (DAF), filtration, GAC and disinfection (Figure 3.6).

The works has a maximum treatment capacity of 220 Ml/d and feeds large parts of Leicester and its surrounding rural areas. As water fed to the Leicester urban area is blended with Hallgates DSRs water, the Ragdale-Wolds segment of distribution system (primarily feeding rural areas and small towns to the east of Leicester) was chosen for investigational purpose. This is fed solely by Melbourne WTW supplied water. Key sites of interest in this area of distribution include Ragdale DSR and BPS, Scraptoft DSR, Oadby DSR and Scalford Road DSR (Figure 3.7).

3.3.3 Campion Hills WTW and its distribution system

Campion Hills WTW supplies Leamington Spa and surrounding areas. Water is abstracted from three sources; Willes Meadow storage reservoir (River Leam water), Campion Terrace borehole and Lillington borehole, and can be supplemented with water from Draycote reservoir. The process flowsheet at the works comprises screening, pre-ozonation, coagulation / flocculation, intermediate ozonation, clarification, filtration, GAC and disinfection (Figure 3.8). Maximum and minimum flows to the works are 45 and 10 Ml/d respectively. Water leaving the WTW is held in a final water storage reservoir before entering distribution. This has a retention time of approximately 20 – 22 hours under normal operating circumstances.

The subsequent DSRs and BPSs in the Priors Marston leg of distribution investigated as part of this study are Ladbrook DSR, Marston Doles BPS, and Priors Marston DSR (Figure 3.9).

3.3.4 Whitacre WTW and its distribution system

Whitacre WTW supplies parts of North Warwickshire and the Coventry systems, via Oldbury and Meriden reservoirs, respectively. Raw water is fed from an on-site reservoir (with a retention time of approximately 24 hours). This receives water from two sources; either directly from the River Blythe, or from the River Bourne, via Upper Shustoke then Lower Shustoke reservoirs sequentially (with a combined retention time of approximately 30 days and capacities of 92 and 192 Ml, respectively). Lower Shustoke can also receive a pumped inflow of up to 90 Ml/d from Whitacre reservoir.

Water treatment at the works comprises coagulation / flocculation, clarification (HBCs), filtration, granular activated carbon and disinfection, with a maximum output of 44 Ml/d (Figure 3.10). Water at the end of the treatment stream is capable of being mixed with treated water from Frankley WTW depending on operational conditions. The DSRs investigated in a stretch of the Nuneaton segment of distribution system were Oldbury DSR No. 1 and No.2 and Tuttle Hill DSR (Figure 3.11).

3.3.5 Draycote WTW and its distribution system

The raw water supplying Draycote WTW is abstracted from the River Leam at Eathorpe and the River Avon, and is stored in an on-site raw water reservoir for up to 12 months. The process flow sheet at the works comprises straining, coagulation / flocculation, clarification (DAF), filtration, granular activated carbon and disinfection (Figure 3.12). Maximum and minimum flows to the works are 50 and 18 Ml/d respectively.

The works supplies the Rugby system and its surrounding rural areas, principally via the Rugby ring main. The leg of distribution isolated for investigation, stretches to the south of Rugby, prior to the water entering the ring main. Within the area studied, Flecknoe DSR, Napton DSR, Napton BPS and Hill BPS were chosen for study (Figure 3.13).

3.3.6 Church Wilne WTW and its distribution system

Church Wilne is located at Church Eaton near to Nottingham. The source water is abstracted primarily from the River Derwent, via two abstraction points. The Draycott intake is downstream of the city of Derby and is preferred by STW over the more distant and hence, more expensive, Little Eaton abstraction point, that is upstream of the city. The intake feeds a raw water storage reservoir on site with a storage capacity of 2791 Ml, which approximates to 20 days storage at the WTW maximum throughput of 135 Ml/d. The process flow sheet at the works comprises screening, coagulation / flocculation (HBCs and DAF - split streams), filtration, GAC and disinfection (Figure 3.14). Maximum and minimum flows through the works are 142 and 20 Ml/d.

Treated water feeds into the Severn Trent Water strategic grid (via the Derwent Valley Aqueduct) and is also distributed into the Bamcote, Strelley and Ladycross DSRs and associated distribution systems, which aid in satisfying a large part of Nottingham and the surrounding areas potable water demand (Figure 3.15).

WTW	Source water	Raw water characteristics
Whitacre	R. Bourne / R.Blythe	Lowland river source. Very high microbial organic matter. High TOC. High bromide.
Melbourne	R. Dove	Lowland river source. Intermediate organic matter character with low variability. Relatively low TOC and bromide.
Draycote	R. Leam / R. Avon	Lowland river source with high bromide concentrations. Relatively hydrophilic, low variability. High TOC.
Campion Hills	R. Leam	Lowland river source. Intermediate organic matter character with low variability.
Church Wilne	R. Derwent	Lowland river source. Relatively hydrophilic, high microbial organic matter with high variability.
Strensham	R. Severn *	Lowland river source. Intermediate organic matter character with low variability. Significant water quality changes, flow rate and quality affected by sewage works discharges and regulated releases from Clywedog management scheme.

Table 3.1; Source water characteristics at each of the six WTWs investigated (* WTW with direct river abstraction).

Figure 3.1; Photograph of Hach hand-held chlorine meters and sample cells.

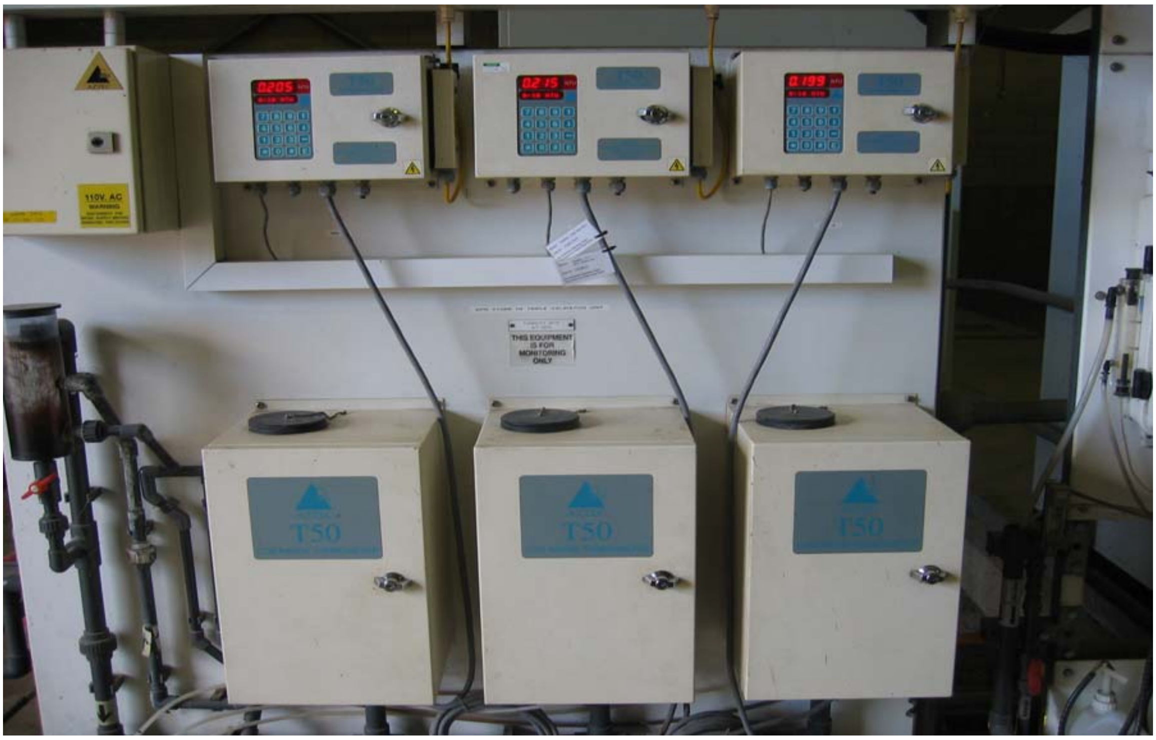


Figure 3.2; Triple-validated turbidity monitoring equipment at Melbourne WTW final water sampling point.

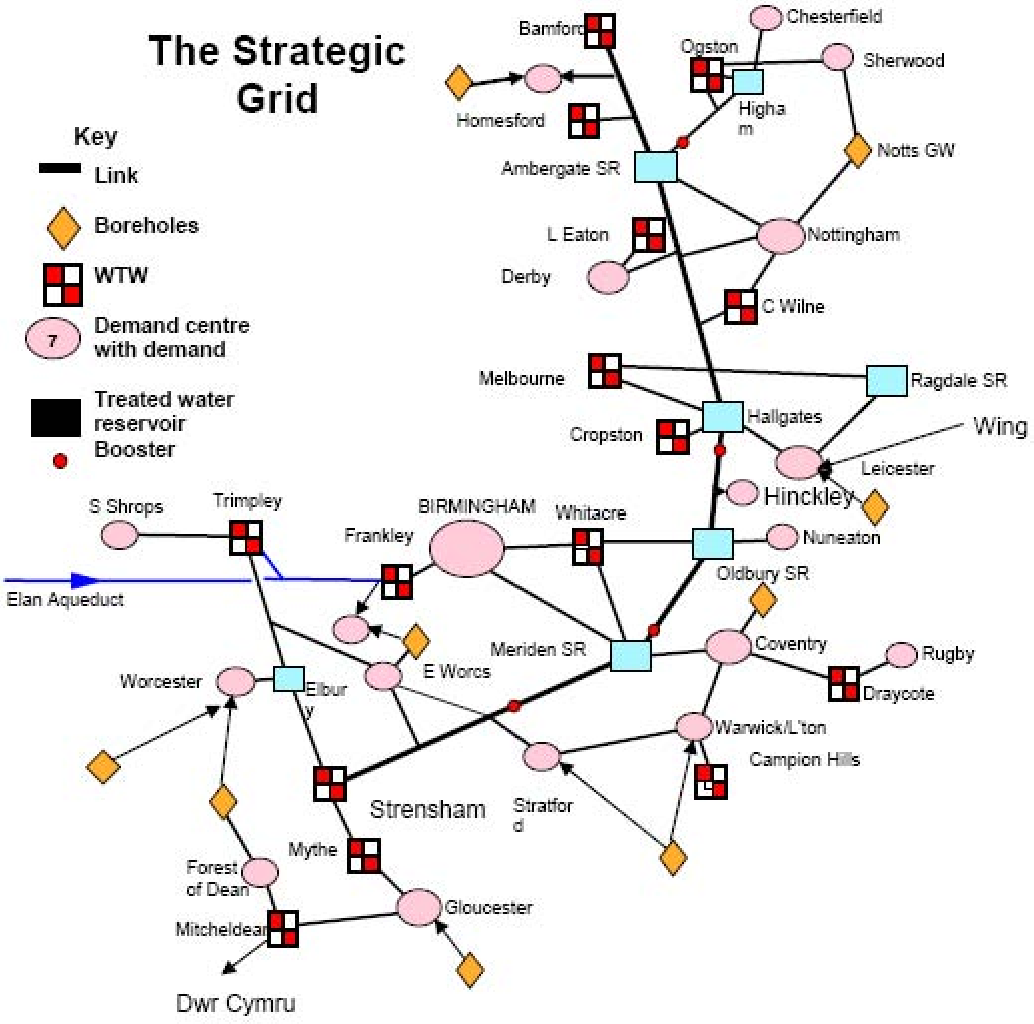


Figure 3.3; Schematic of the Severn Trent Water strategic grid (as shown on STW website - www.stwater.co.uk).

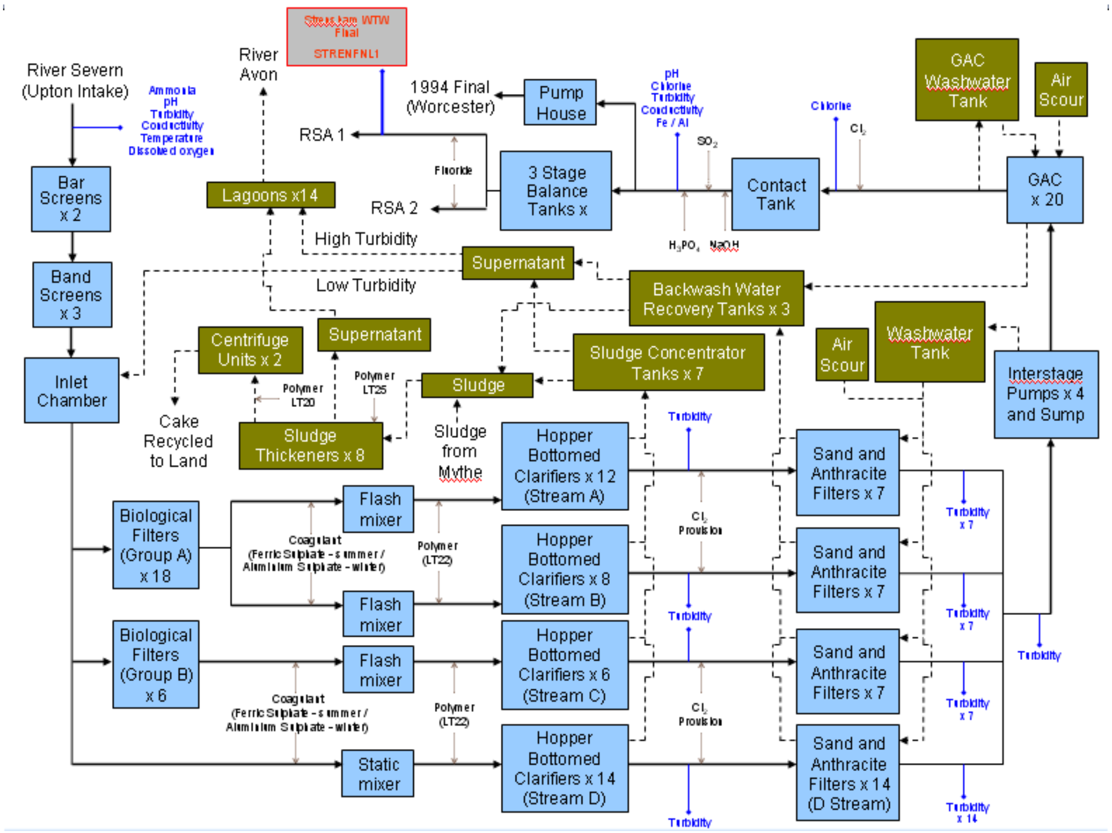


Figure 3.4; Process flow sheet of Strensham WTW.

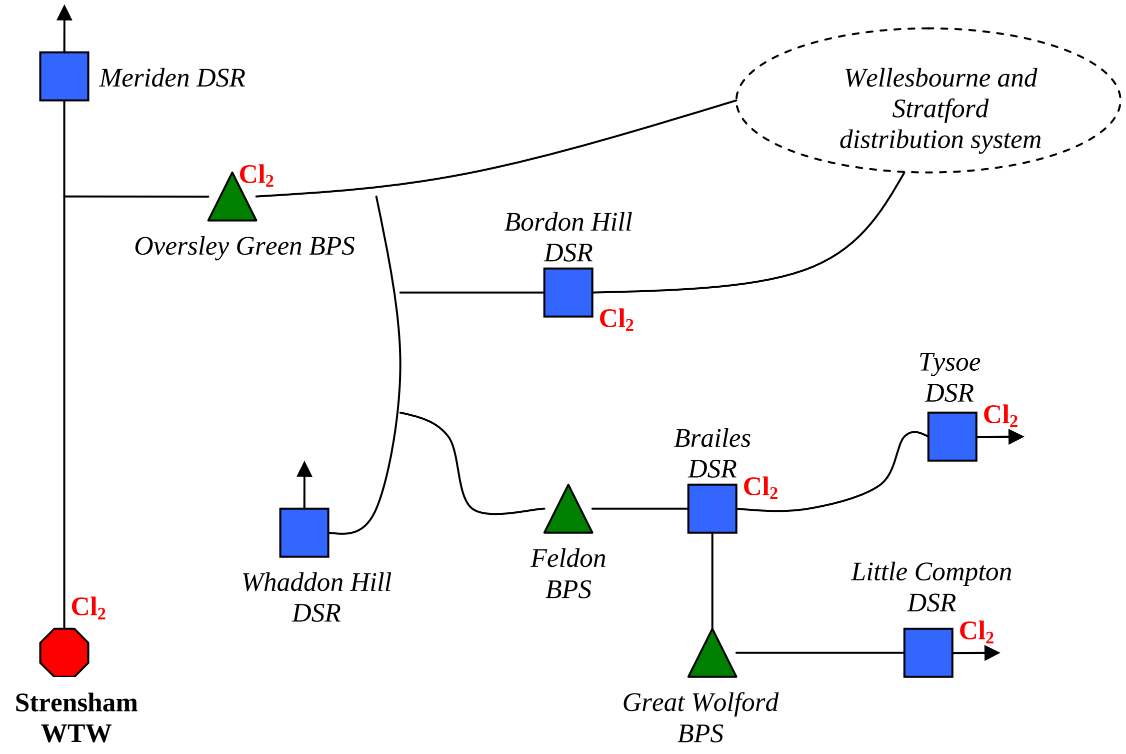


Figure 3.5; Schematic of Strensham WTW distribution system (Shipston zone).

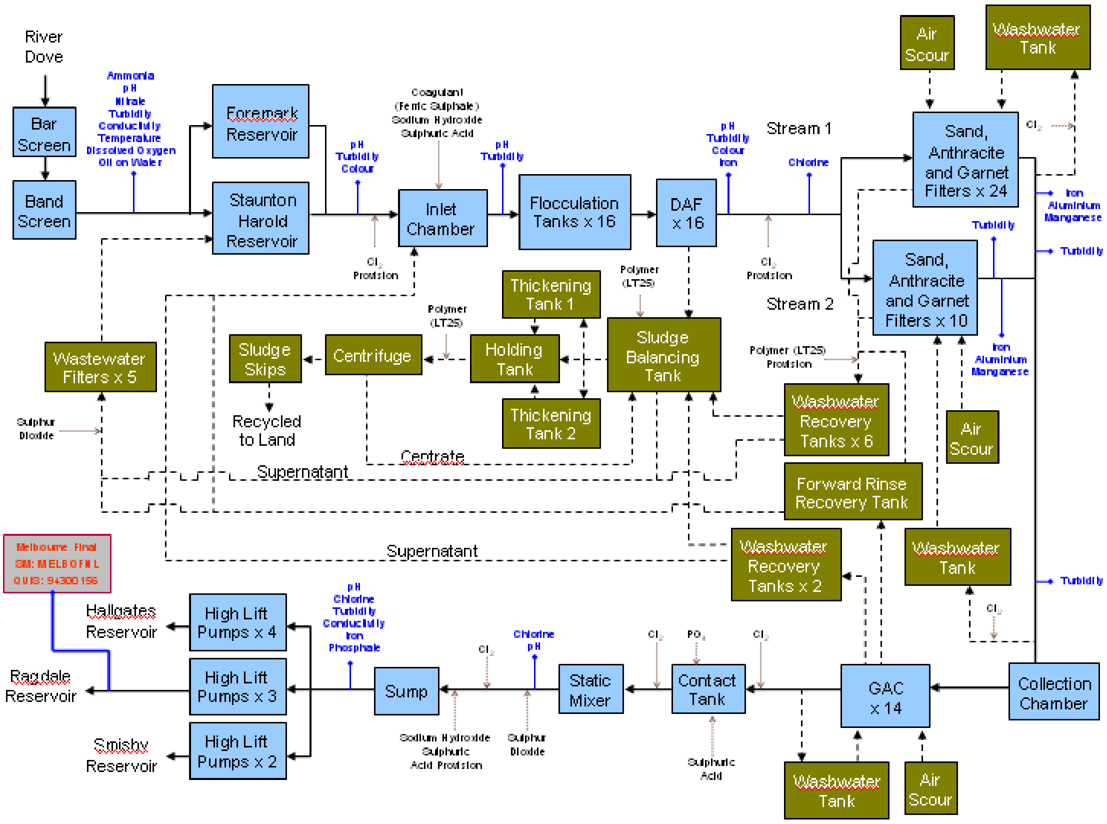


Figure 3.6; Process flow sheet at Melbourne WTW.

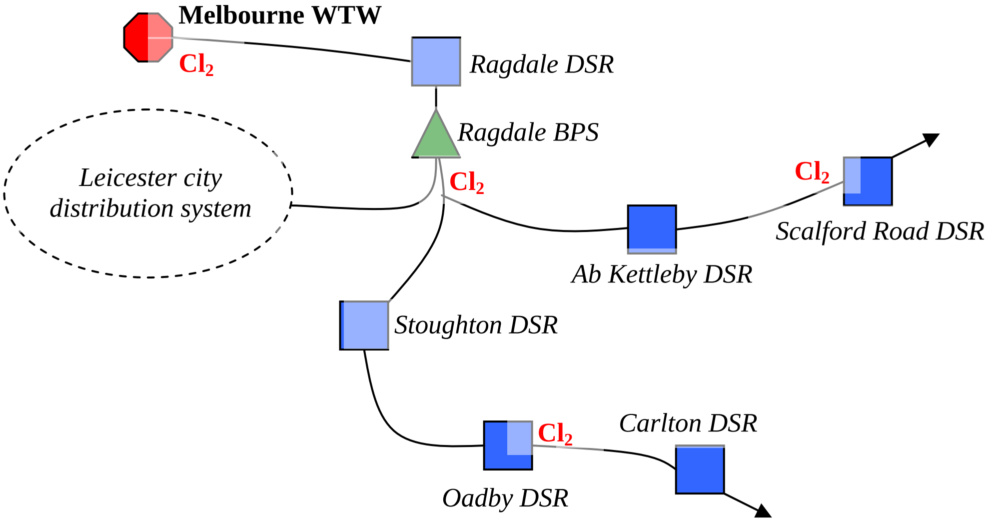


Figure 3.7; Schematic of Melbourne WTW distribution system (Ragdale-Wolds zone).

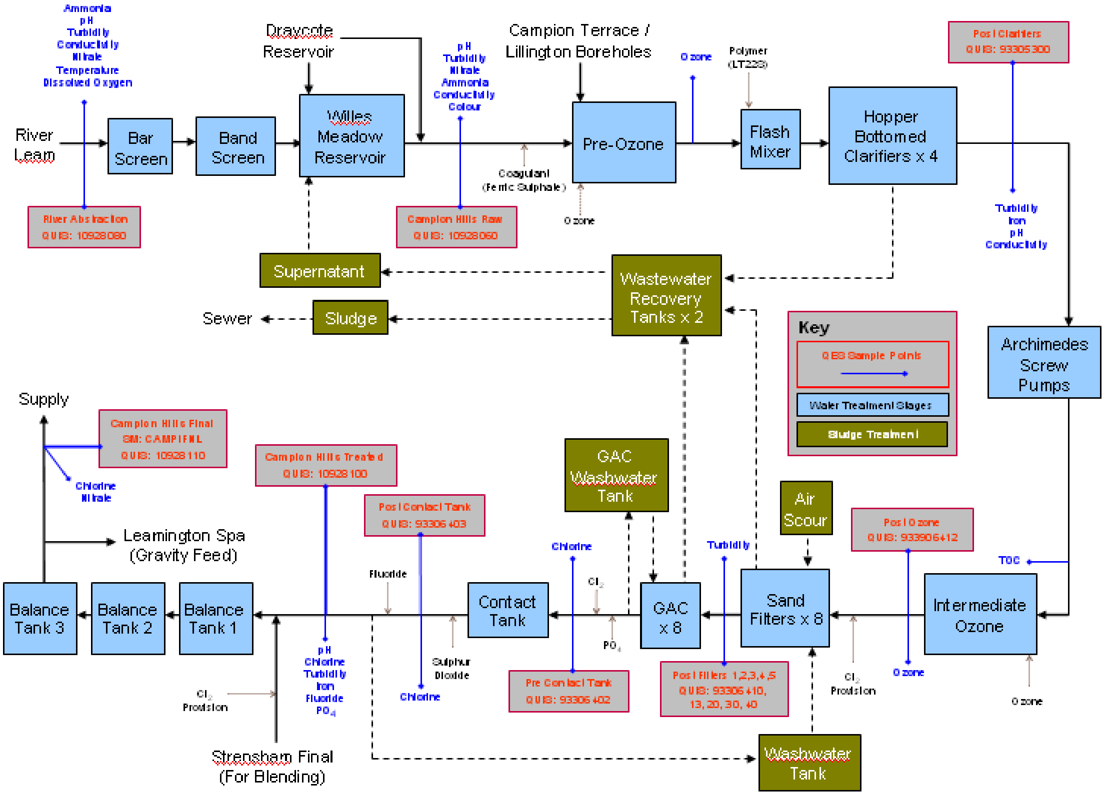


Figure 3.8; Process flow sheet at Campion Hills WTW.

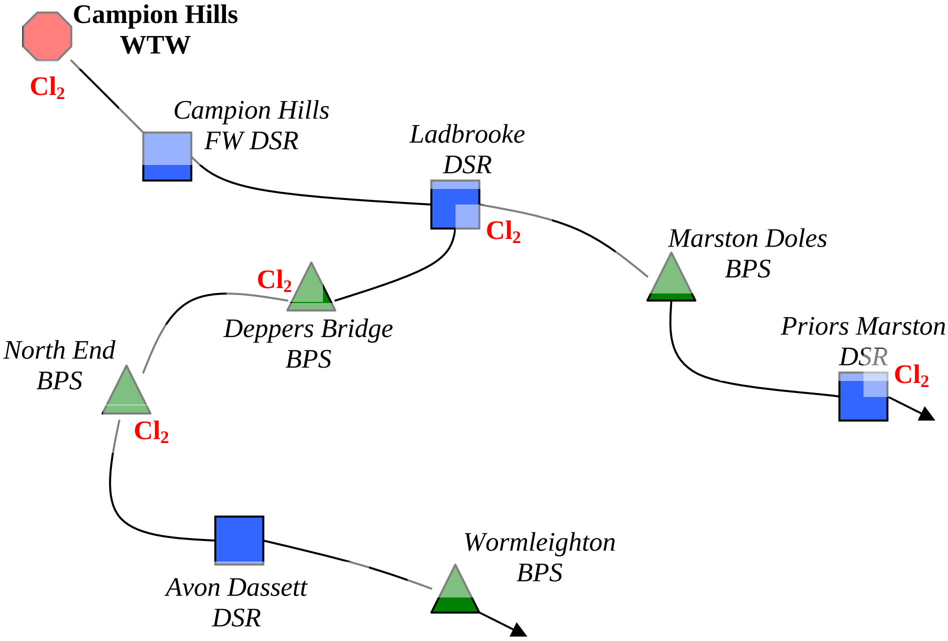


Figure 3.9; Schematic of Campion Hills WTW distribution system.

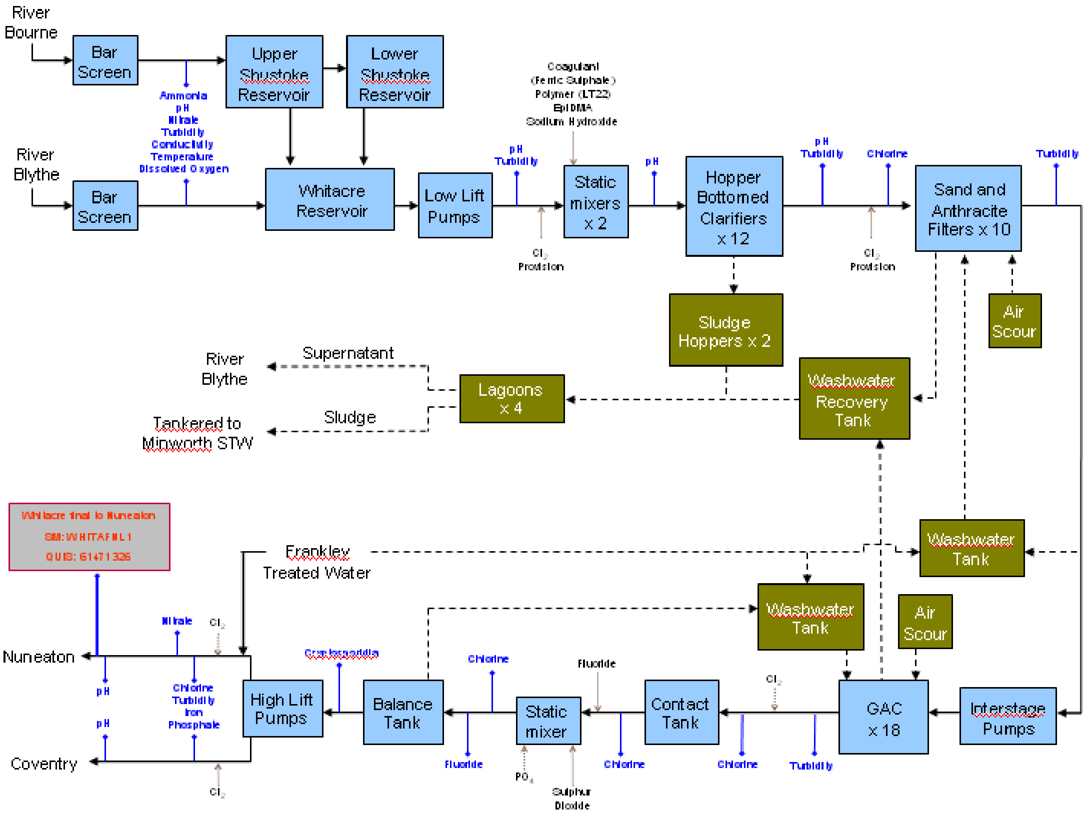


Figure 3.10; Process flow sheet at Whitare WTW.

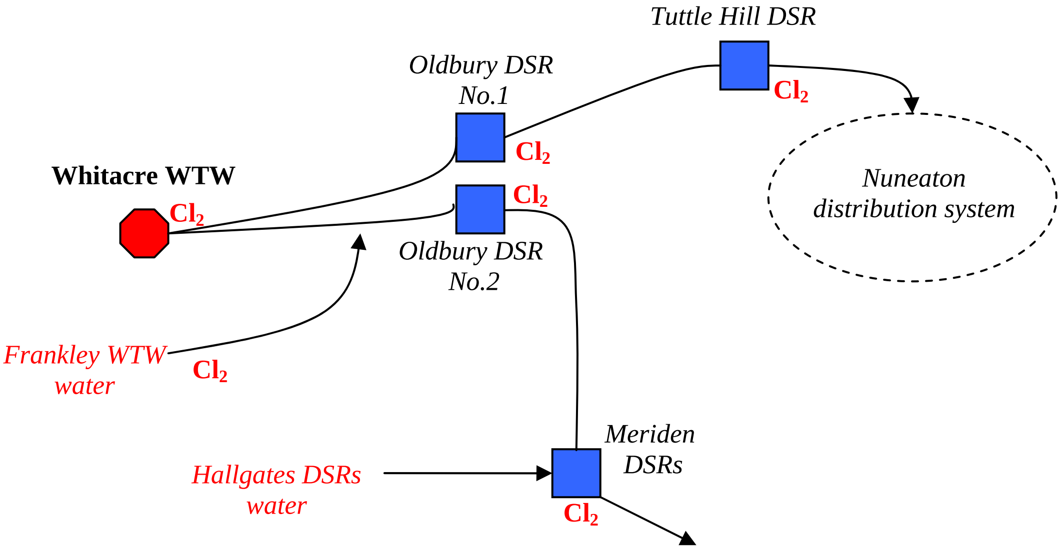


Figure 3.11; Schematic of Whitacre WTW distribution system.

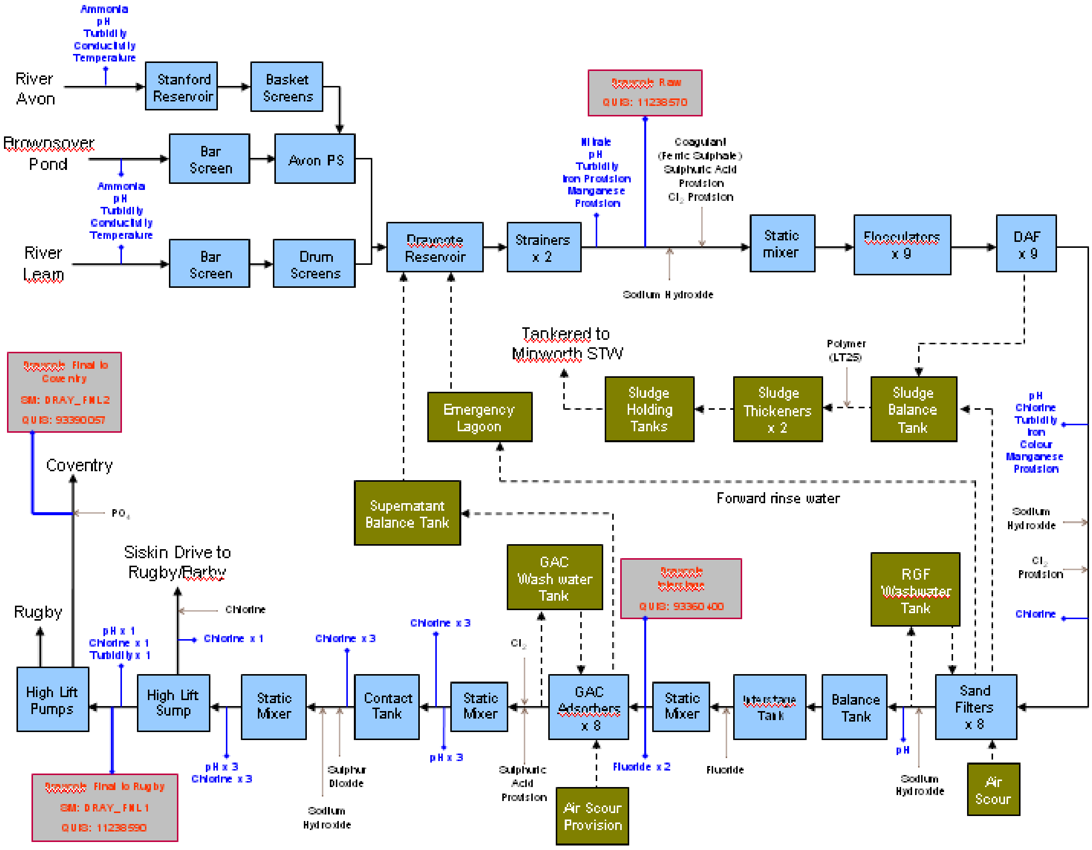


Figure 3.12; Process flow sheet at Draycote WTW.

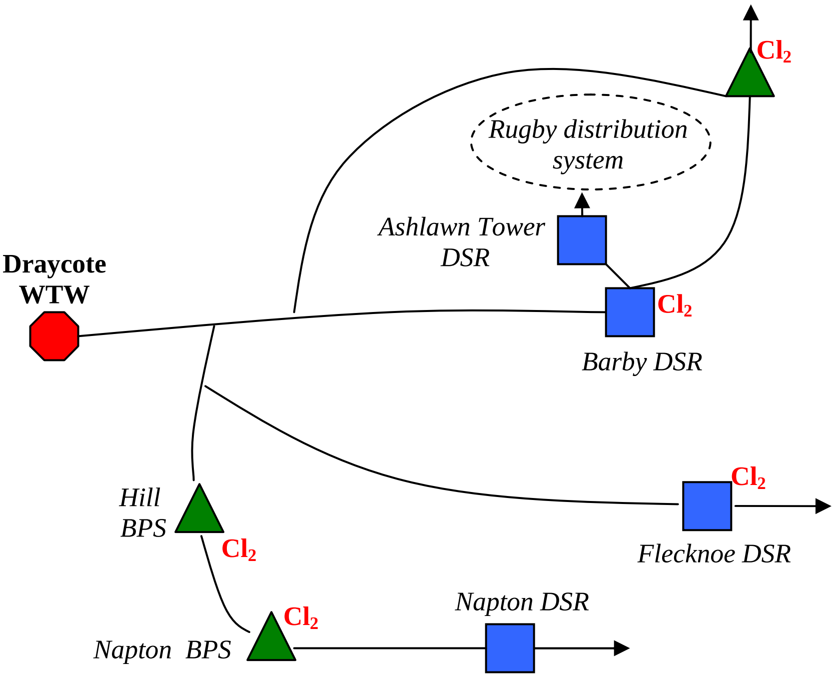


Figure 3.13; Schematic of Draycote WTW distribution system.

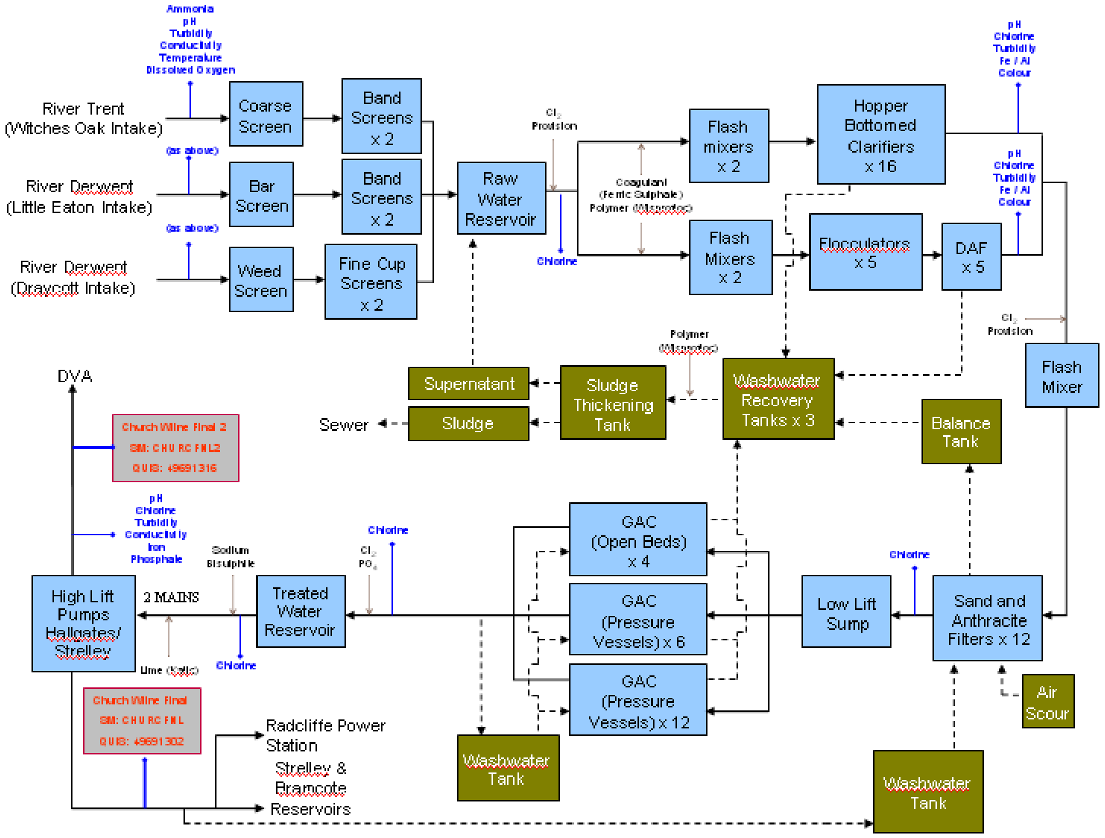


Figure 3.14; Process flow sheet at Church Wilne WTW.

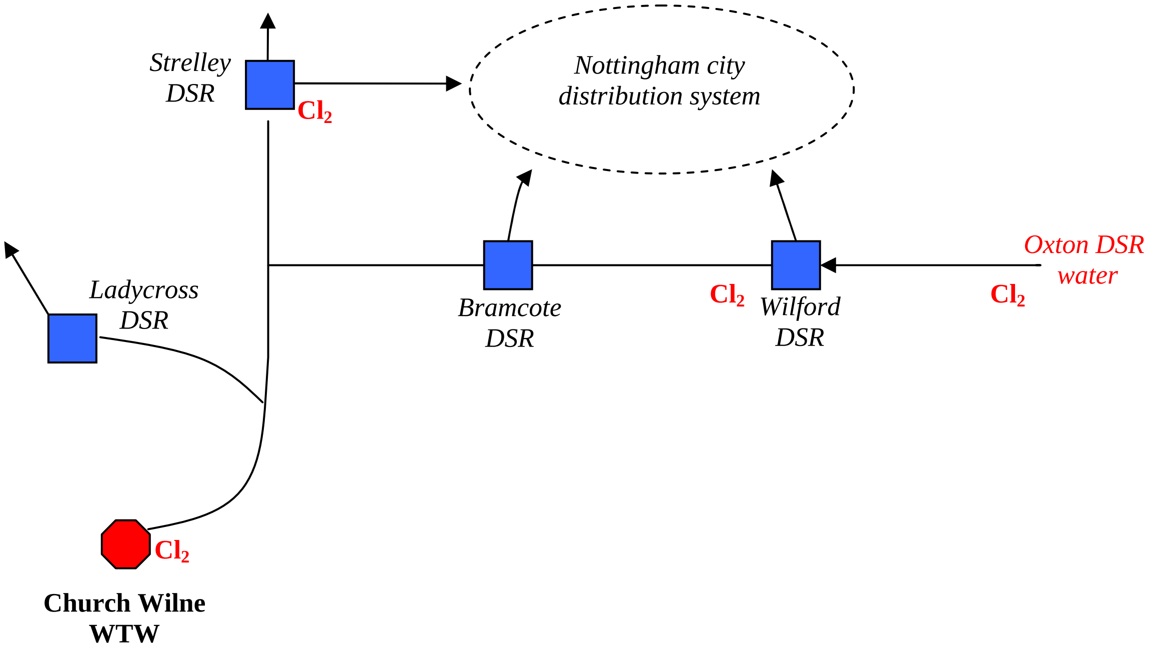


Figure 3.15; Schematic of Church Wilne WTW distribution system.

Chapter 4 System Response

4.1 Introduction

It has been demonstrated that THM formation depends upon numerous factors. Principally, the applied chlorine dose, retention times in unit processes and pipes, temperature, input water quality (pH, organic and inorganic content) and changes in the water chemistry are known to influence the rate, speciation, and location of THM generation (Amy *et al*., 1987; Singer, 1994; Clark & Sivaganesan, 1998; Latifoglu, 2003; Liang & Singer, 2003; Toroz & Uyak, 2005). Accordingly, the management of THMs involves the assessment and mitigation of factors contributing to their formation from raw water to customer tap.

The inter-system and temporal variations in TTHM concentrations at the six WTW final waters between January 2007 – September 2008 is displayed in Figure 4.1. Average TTHM concentrations range from 16.4 to 32.9 µg/l (s.d. ~ ± 4.9 to 8.0 µg/l), with a significant seasonal trend evident at each of the six WTWs (a two fold increase in summer concentrations compared to winter concentrations is apparent). The purpose of this chapter is to explore these variations as a response to the above factors with the aim of quantifying where and when THMs are formed in each of the systems, thus determining the causative factors. Analysis from this Chapter will provide the foundations for, and focus the direction of, work in subsequent Chapters, and ultimately will aid the development of operational modelling work.

The work in this chapter focuses on objective (i) from Chapter 1:

- ***To undertake a detailed analysis and cross comparison of THM formation and chlorine decay in six water supply systems, relating the differences to WTW operational and source water characteristics, supply procedures, and temporal and spatial variation in order to try and understand critical factors in each of the six systems.***

4.2 Survey details and sources of data

The data portrayed have been collected from three main sources; data collected during sampling campaigns designed as part of this study, STW routine data, and data from previous UoB studies at the relevant sites of interest.

Data from routine sampling carried out by Severn Trent Water in each of the six WTWs and distribution systems were collected over a five year period from 2003 to 2008. These data included TOC, UV_{254} absorbance, temperature, pH, confirmed coliform failures, coagulant dose, turbidity, bromide, THM, free and total chlorine. The majority of these sample results were from WTW raw and final waters, and from DSR outlets, as these are of most concern to a water company from a regulatory standpoint.

To increase the spatial resolution of these samples, a series of sampling and corresponding laboratory work were carried out on various dates through each of the six WTWs and their respective distribution systems. The type and number of samples typically taken on each sampling day are outlined in Table 4.1 and detail of the applied methodology can be found in Chapter 3.

Of the six WTW studied, Strensham is the only one to be fed directly from a river source (R. Severn), and hence showed greater fluctuations in raw water quality, which is likely to present the most potential problems for investigating the effects on THM formation. Consequently, the majority of the analyses and discussion have been focussed on this, the most academically challenging, site. Cross analysis between all six WTWs and their respective distribution systems is then made towards the end of the chapter. A similar approach is adopted in subsequent chapters for the same reason.

4.3 Strensham WTW and distribution system

4.3.1 River Severn flow data

As a consequence of being fed by direct river abstraction, Strensham WTW operations and performance are in some way governed by, and are vulnerable to, fluctuations in river water quality. It is therefore important to understand how water quality varies in the river seasonally and on a shorter time frame, both of which are principally governed by river flow.

Saxons Lode is a river flow measurement station (operated by the Environment Agency) within a few hundred metres of the abstraction point (Figure 4.2). Daily averages of river flow are shown in Figure 4.3 between 2003 and 2008. The variability in flow is substantial (ranging from 994 to 43,804 Ml/d), with an average of 7139 Ml/d (s.d. ~ 7345 Ml/d).

Although flow typically follows a seasonal pattern, with flows during the winter being approximately three times higher than flows in the summer months, high flow peaks occur through out the year following substantial precipitation events over the extensive catchment area (6853.2 km^2) upstream of the station (FEH Catchment Descriptors, 1999); a notable example being the notorious summer 2007 floods (highlighted in Figure 4.3), where the highest flows in the studied period were recorded.

4.3.2 Raw water organic content

Natural organic matter (NOM) has long been considered as the primary precursor to disinfection by-product formation (Rook, 1974; Kitis *et al.*, 2001; Goslan, 2003). NOM is a complex mixture of organic compounds (generated from decaying vegetation, organic soils and other biological activity in a water body and the surrounding watershed) that is present in all natural waters. As a result of its heterogeneous and undefined character, along with analytical techniques to fractionate and isolate different segments being complex, expensive and impossible to monitor routinely, the amount of NOM is commonly measured through surrogate parameters such total organic carbon (TOC), dissolved organic carbon (DOC), or ultraviolet absorbance at a wavelength of 254 nm (UV_{254} absorbance).

STW routine samples of TOC and UV_{254} absorbance in the raw water are shown in Figure 4.4, for the period 2003 to 2008. Both parameters reflect the broad variability attributed to direct abstraction from a river source. TOC concentrations average 5.44 mg/l, ranging from 2.75 to 10.49 mg/l (s.d. ~ 2.02 mg/l). UV_{254} absorbance concentrations range from 0.05 to 0.65 cm^{-1} and average 0.25 cm^{-1} (s.d. ~ 0.16 cm^{-1}). No significant seasonal variation can be identified, with the combined winter average (October – end of April) for all years (TOC ~ 5.31 mg/l / UV_{254} ~ 0.26 cm^{-1}), being similar to the combined summer average (May – end of September) for all years (TOC ~ 5.59 mg/l / UV_{254} ~ 0.22 cm^{-1}).

This is consistent with observations made of another lowland river by Bridge (2005), who found surrogate organic concentrations in the River Trent (a raw water source for Church Wilne WTW) to be consistent throughout the year. In contrast, a noticeable seasonal variation was observed in the raw water of Bamford WTW (fed by upland waters), where organics peaked in autumn / winter months (Roberts, 2004). Noticeable seasonal variation was also observed in previous surface water studies by other researchers (*e.g.* Toroz & Uyak, 2005; Rodriguez *et al.*, 2007; Uyak *et al.*, 2008).

Figures 4.5 and 4.6, show TOC and UV_{254} absorbance concentrations to display a similar temporal trend with flow. Positive linear relationships between flow and the two parameters are reasonable (Figures 4.7 and 4.8) considering 136 points were analysed (R^2 ~ 0.21 for TOC & 0.61 for UV_{254}, both significant at the 1 % level). Hydrologic conditions define the flow paths that water takes in transporting materials to the river and determines interaction with soil horizons of differing character. The positive relationship would thus be anticipated as rain events can lead to the flushing of the upper soil horizons and transport recently deposited organic compounds to surface waters (Aiken & Cotsaris, 1995; Reckhow *et al*., 2004). However, there are other significant processes that may influence the organic load in the river that leads to the correlations to be skewed. Load usually transported from rural and urban colloids and the considerable variability shown is possibly due to the flushing out of material during the earliest stages of the river flow hydrograph and possibly low flow eutrophic activity.

As a basic approximation (from Figure 4.7), an increase in the river flow from 2,000 to 35,000 Ml/d leads to an increase in raw water TOC concentrations from 4 to 8 mg/l. This represents a substantial (35 fold) increase in the actual load of organics in the river water.

Raw water turbidity and colour can also be seen to relate temporally with river flow (Figure 4.9). Both have a positive relationship with flow (Figure 4.10), with correlation being stronger with turbidity (R^2 ~ 0.45, significant at the 1 % level) compared to colour (R^2 ~ 0.14 significant at the 15 % level). An increase in turbidity would typically coincide with an increase in flow, as fine solids are flushed from the surrounding catchment into the river. The relationship with colour is more complicated as it is more likely influenced by seasonal factors (*i.e.* peaks can be seen in Autumn with the decomposition of vegetation in the surrounding catchment).

Figure 4.4 shows raw water TOC and UV_{254} absorbance concentrations to follow a similar path temporally. Figure 4.11 shows the linear correlation between the two to be reasonable in the raw water (R^2 ~ 0.60, to a level of 1 % significance), with the scatter accounted for by the differences between the organics represented by the surrogates and the plausible changes in the concentration and nature of them temporally. Volk and co-workers (2005) reported the strength of relationship between UV_{254} absorbance and TOC / DOC to diminish under changing hydrological regimes, suggesting that sources of organics and their attributes change with shifting hydrological conditions (Volk *et al*., 2005; Uyak *et al*., 2008).

4.3.3 Raw water inorganic content

Inorganic particles found in natural waters may be natural or may be anthropogenic in nature. One such substance, which has a particular significance concerning the formation of THMs, is the anion bromide (Br^-). Natural sources of bromide include geologic erosion and salt water intrusion (Carns & Stinson, 1978, Magazinovic *et al*., 2004), while anthropogenic sources include agricultural runoff, sewage treatment and salts used for de-icing roads (Luong *et al*., 1980, Myllykangas *et al*., 2003).

Between January 2003 and October 2008, raw water bromide concentrations varied between 51.1 and 130.5 µg/l (Figure 4.12). With an average of 93.7 µg/l, they are slightly higher than the mean concentration of approximately 70 µg/l found in a study of river waters in Europe (Legube, 1996), but slightly lower than the mean concentration (105 µg/l) observed in a study by Sohn *et al*. (2006) of a range of surface water samples taken from different states across America.

A stronger relationship (compared with organics) was observed between bromide and flow, with both inverse linear ($R^2 \sim 0.53$) and power ($R^2 \sim 0.67$, both significant to a 1 % level) relationships providing reasonable fits with the data (Figure 4.13). The relationship will be governed by a combination of dilution of groundwater inputs, and of urban inputs from sewage treatment works outfalls and combined sewage overflows (CSO). An approximate six-fold increase in load results from an increase in flow from 2,000 to 35,000 Ml/d, indicating river flow has a more substantial influence on increasing organic load in the river in comparison to quantities of bromide. It is fortunate, in terms of the influence on THM formation, that the relationships of carbon and bromide with flow are positive and negative respectively, meaning bromide is low flow critical and carbon high flow critical.

With point source inputs being reasonably predictable, the concentration of bromide and organics in the raw water could potentially be relatively straightforward to predict using flow data that are available every 15 minutes from the river gauging station at Saxons Lode.

4.3.4 Temperature

Temperature can be seen to vary seasonally between 4 and 25 °C in the raw water (Figure 4.14). Average temperatures in the summers of 2007 and 2008 were not as high as in previous summers in the study period (Table 4.2). In comparison to the chemical characteristics of the water, temperature is easier to assess, predict and subsequently model. Its effect on chlorine consumption and THM formation will be discussed in sections 4.4.3 and 4.4.4, respectively. Temperature levels are not likely to vary through the WTW as treatment processes are not likely to induce any significant temperature change. On the other hand, temperature may vary in distribution, dependant on proximity of water in storage and pipes to the surface, and its time spent there (Mays, 1999).

4.4 Variation in water quality through Strensham WTW

The variation in raw water quality will have a profound influence on the formation of THM upon contact with chlorine. However, prior to the introduction of oxidants to the water, significant adjustment can be made to the water, enabling the quantity of potential precursor material to be reduced (section 2.12.2). These changes are governed by water's propensity to effective treatment and also WTW operational procedures. These factors will be discussed in the following section.

4.4.1 Organic content

NOM is important in the water treatment process not only due to its role as DBP precursor material, but also because it transports inorganic and organic pollutants (Collins *et al.*, 1986), it may act as a source of nutrients for microorganisms to grow in the treatment unit or distribution system (Siddiqui *et al.*, 1997; Khan *et al.*, 1998), it may cause discoloration of the water, and it will compete with other organic and inorganic compounds which are amenable to adsorption by GAC (Fabris *et al.*, 2008). Today, the majority of DBP control strategies (*e.g.* coagulation, clarification, filtration, carbon adsorption, membrane techniques) focus on organics removal prior to disinfection. In general, TOC is used as criterion for organics / DBP precursor removal effectiveness. The USA regulation mandates water treatment plants using chemical disinfectants to remove predetermined levels of TOC as a means of reducing DBP precursors and recognizes enhanced coagulation as the best available technology for achieving this (USEPA, 1998).

To investigate the organics removal through the WTW, TOC samples were taken at the raw, post-clarifier, post-RGF, post-GAC and final water sampling points to allow for greater spatial resolution to be added to the samples routinely taken by STW at the raw and final waters (Figure 4.15).

Results from the 18.03.08 sampling date appear anomalous in comparison to the other results and do not coincide with routine STW samples at the raw and final water around this date, suggesting possible problems with sampling / laboratory analysis. For this reason they are omitted from the discussion in this section. The other results are more akin to the available raw and final water STW data around the pertinent dates.

The greatest removal of TOC occurred across the clarification stage (Figure 4.16) where between 22 and 59 % (average ~ 32 %) of the raw water concentration (averaging 4.17 mg/l TOC) was removed. This accounted for approximately 60 to 80 % of the total reduction in TOC concentrations between the raw and final water sampling points. These figures are in line with those observed in previous studies at other STW WTWs (Hua, 1999; Courtis, 2003).

TOC removal across the filtration process was small (average of 9 % reduction in inlet concentrations). This would be anticipated as filtration is known to remove only a small portion of unbound NOM. Filtration primarily removes NOM through removing flocculated particles that contain NOM-bound material (Westerhoff & Chowdhury, 1996), with its effectiveness dependant primarily on head-loss, filtration rate, backwash regime and media surface chemistry (Matilainen *et al*., 2006).

Limited removals of TOC were also observed across the GAC unit process (average of 15 % reduction in inlet concentrations). GAC is primarily employed in water treatment for the removal of micro-pollutants such as pesticides, industrial chemicals, taste and odour compounds and algal toxins (Newcombe, 1999; Matilainen, 2006), rather than for the specific removal of general organic compounds. Courtis (2003), however, showed the effectiveness of fresh or regenerated GAC at removing up to 66 % of TOC concentration in regeneration studies at Church Wilne WTW. Roberts (2004) also observed an impact of GAC age on rates of TOC removal, with GAC approximately 18 months old removing between 5 – 15 % of TOC, whereas 3 month old GAC removed between 40 – 50 % of inlet TOC concentrations. This aids explanation of the inconsistent efficiency between sampling days in this study (6 – 29 %), with the GAC media known to be regenerated on an operational basis at different times of the year.

Final water TOC and UV_{254} absorbance concentrations between 2003 and 2008 are shown in Figure 4.17. A moderate decrease in both parameters was observed over this time period. This will be a result of either a change in WTW performance, raw water quality, or both. No significant decline in raw water TOC concentrations was observed (section 4.2.2), implying an improvement in WTW performance.

Figures 4.18 and 4.19 display the percentage removals of TOC and UV_{254} absorbance concentrations between the raw and final waters (between 2005 and 2008). Percentage TOC reduction varied temporally between 40 and 80 % (average ~ 55 %), and slightly increased over the time period. A minor increase was also observed in UV_{254} absorbance removal rates. UV_{254} absorbance removals ranged between 63 and 94 % and on corresponding dates the

UV_{254} absorbance material was always removed to a greater extent than TOC. This supports observations in previous research (Edzwald *et al.*, 1985; Crozes *et al.*, 1995; Matilaninen *et al.*, 2006; Uyak & Toroz, 2007; Uyak *et al.*, 2008).

Also shown in Figures 4.18 and 4.19 is the coagulant dose being applied to the water over the same time period. Coagulation has historically been used for the control of particles in drinking water, and its role in the simultaneous control of organic carbon is well known (Owen *et al.*, 1993; Teksoy *et al.*, 2008). Figures 4.20 and 4.21 show the WTW operational response of increasing coagulant dose to an increase in turbidity and UV_{254} absorbance in raw water, both of which are measured online, allowing changes in water quality entering the WTW to be rapidly identified.

A positive linear relationship between coagulant dose and removals of both TOC (R^2 ~ 0.43 significant at the 1 % level), and UV_{254} absorbance (R^2 ~ 0.40, significant at the 1 % level) were observed (Figure 4.22). The correlation will not be accurate due to inconsistencies associated with the performance of other WTW unit processes over the studied period (*e.g.* coagulation pH, GAC age, composition of organics and inorganics). However, it does provide a useful guide in predicting approximate removals of the two surrogate organic parameters to coagulant dose between raw and final waters. From the relationships shown, it would be indicative to say that an increase in coagulant dose by 1 mg/l would lead to a 10 % and 8 % increase in the removal of TOC and UV UV_{254} absorbance removals, respectively, between the raw and final waters.

In order to maximize the removal of particles and organics, the coagulation pH needs to be considered. The maximum removal of organics occurs when coagulation is performed at the optimum pH for the coagulant under consideration (van Leeuwen *et al*., 2005). A decrease in pH has been shown to increase the removal of TOC (Randtke, 1988; Crozes *et al.,* 1995; White *et al*., 1997; Volk *et al.,* 2000; van Leeuwen *et al*., 2005; Uyak & Toroz, 2007), whereas an increase in coagulant dose will increase the number of available sites for the attraction of particles. Chowdhury *et al*. (1995) reported that baseline plant conditions removed 9 % of the TOC (initial TOC = 2.4 mg/l), but TOC removal increased to 25 % when carbon dioxide was added to lower the pH from 8.0 to 7.0. At Strensham WTW, in parallel with the increases in coagulant dose, the coagulation pH is also lowered at similar times, as highlighted in Figure 4.23. Unfortunately no regular source of organics data is available from the pre- and post-clarifier sampling points to clarify the effects of changing the coagulant dose and pH in more detail and further investigational work is therefore required.

As with Hua’s (1999) work at Frankley WTW and Melbourne WTW, it was observed that some of the sampling day TOC concentrations were higher in the final water samples in comparison to the preceding post-GAC samples (Figure 4.15). This is likely to be a result of samples being collected at different times during the sampling day which, when coupled with varying retention times across unit processes, meant the water was of different quality. It has however been reported that some oxidising agents, including hypochlorous acid, may lead to an increased TOC response in analysis due to the oxidation of traces of residual carbonaceous material in these compounds (STL analytical method statement, 2008).

The relationship between TOC and UV_{254} absorbance in the final water was not as significant in the final water ($R^2 \sim 0.21$, significant at the 5 % level) as the raw water noted earlier (Figure 4.11). This will be due to varying degrees of removals of the organic constituents through the treatment process and the different components the surrogates represent.

4.4.2 Inorganic content

Bromide occurs as a dissolved species in water and cannot be readily removed by precipitation. It is also not readily removed by coagulation and associated solid-liquid separation processes and therefore tends to pass conservatively through conventional treatment processes (Westerhoff *et al*., 2004; Bonacquisti, 2006). This justifies the modest reductions in bromide concentrations observed between the raw and post-GAC water on the sampling days (Figure 4.24).

Even though the bromide ion concentration may be seen to decrease across the WTW, the total bromine concentration (including both organic and inorganic bromine compounds and their associated conversion products) does, in fact, remain at the same level. Between the post-GAC and final water sampling points there is a larger reduction in bromide concentrations in comparison to the preceding sections of the WTW (ranging between a 26 % and 43 % reduction in post-GAC inlet concentrations). This indicates a change in the composition of total bromine, caused by the reactions occurring during the chlorination process (*i.e.* formation of halogenated by-products such as brominated THMs).

There have been numerous studies that have investigated the effect of water treatment processes on bromide, in particular relating to the effect of the chlorination process (Ichihashi *et al*., 1999; Nokes *et al*., 1999; Elshorbagy *et al*., 2000; Chang *et al*., 2001; Myllykangas *et al*., 2003; Magazinovic *et al*., 2004; Westerhoff *et al*., 2004; Sohn *et al*., 2007; Fabbricino & Korshin, 2009). Chlorination in the presence of bromide ion, has been shown to lead to the formation of more brominated and mixed chloro-bromo derivatives. Bromide will not react directly with NOM, but can be oxidized by chlorine to hypobromous acid (HOBr) or hypobromite ions (OBr^-) with the relative quantities of each depending on the prevailing pH (HOBr favouring acidic and OBr^- favouring alkaline conditions). These subsequently react with NOM to produce a variety of organ-halogenated by-products. The effect of changes in bromide concentrations on THM formation will be discussed briefly in section 4.4.5 and will be explored in more detail in chapter 6.

4.4.3 Chlorine

Chlorination is employed at each of the WTWs considered to ensure effective inactivation of any bacteria remaining in the water after physical and biological treatment. At Strensham WTW, water leaving the contact tank is then de-chlorinated with sodium bisulphite to reduce chlorine concentrations to a suitable concentration before going into distribution. Free chlorine concentrations at each of these stages are shown temporally between October 2003 and September 2008 in Figure 4.25.

Noticeable adjustments in WTW chlorination procedures are evident. First and foremost, the suspension of pre-chlorination at the WTW in late June 2004 and the corresponding reduction in the pre-contact tank set point chlorine concentration leads to a decrease of approximately 0.6 mg/l at the pre-contact tank stage. Free chlorine concentrations then remain stable around the 2.1 mg/l set point concentration until another fall in the spring of 2006, where concentrations decline in the region of 0.2 mg/l. From then until the end of the studied period (September 2008) concentrations remain relatively stable with an average of 1.92 mg/l (s.d. ~ 0.10 mg/l). Over this same period (March 2006 – September 2008) outlet free chlorine concentrations average 1.58 mg/l (s.d. ~ 0.12 mg/l), representing a consumption of approximately 0.35 mg/l free chlorine across the contact tank.

Chlorine is a non-selective oxidant and will therefore react with both organic and inorganic substances in water in different degrees. Consumption is governed essentially by the type and quantities of these constituents (chiefly the ammonia concentration), and variations in raw water quality and treatment processes described above will help explain some of the variation in chlorine demand across the contact tank. As with most chemical reactions the rate is determined not only by the type and quantity of these reactants but also the water temperature. Chlorine consumption is observed to increase in the summer months when temperature is higher (Figure 4.26), leading to an approximate consumption of 0.38 mg/l in the summer months (May – September) compared to 0.30 mg/l in the winter months (October – April). Unfortunately, the lack of regular organic and bromide data through the WTW mean the relationship between these parameters and chlorine consumption is difficult to quantify. This will be explored further in the controlled laboratory tests detailed in Chapter 5.

De-chlorination of the water lowers the chlorine concentration to an average of 0.50 mg/l (s.d. ~ 0.07 mg/l) and by the time the water has passed through balancing tanks and is fed into the distribution system, chlorine concentrations average 0.44 mg/l (s.d. ~ 0.04 mg/l) at the WTW final water sampling point. Free chlorine concentrations at this point equate to approximately 80 % of the total chlorine concentration in the water.

4.4.4 THM

THMs include chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$) and bromoform ($CHBr_3$), the sum of which is denoted as total THMs (TTHM).

TTHM concentrations in the final water between 2003 and 2008 are displayed in Figure 4.27. Short-term variation in TTHM concentrations is gradual. There is noticeable seasonal variation with summer concentrations being approximately double the winter concentrations in the corresponding year.

It is clear that TTHM concentrations decline over this period to which the variations in raw water quality and treatment processes considered in preceding sections will contribute to in varying degrees. Figures 4.28 and 4.29 show that the trend in final water TOC concentrations and, most notably, temperature, follow a similar pattern to TTHM concentrations, with positive linear relationships observed with each parameter (Figure 4.30). However, the correlations (R^2 values) are limited, particularly for TOC (TOC ~ 0.21 / Temperature ~ 0.49, both significant at the 1 % level), due to the wide ranging variables underlying the nature of the water and the quality of treatment conditions.

Spot samples on the sampling days showed that an average of 77 % of the TTHM formed across the WTW is formed by the post-contact tank stage. THM concentrations on the summer sampling days (Figure 4.31) were over double the concentrations observed from the Spring sampling days (Figure 4.32), which is consistent with typical concentrations in routine final water samples between the two periods. The predominant cause of this difference will be due to temperature differences, although any variations in the physiochemical nature of the water between sampling days will also play a significant role. These aspects will be discussed in greater detail when different factors are isolated under laboratory conditions in chapters 5 and 6.

4.4.5 Speciation of THM

$CHCl_3$ is frequently seen as the predominant species in studies of THM concentrations in drinking water (McGuire *et al*., 2002; Gang *et al*., 2003a; Rodriguez *et al*., 2007; Baytak *et al*., 2008). Courtis' (2003) study of final water THM concentrations between January 1997 and December 1999, also found $CHCl_3$ to be the principal THM species at four out of the six STW WTWs investigated (including Strensham WTW).

$CHCl_3$ was also the predominant species in 2003 at the final water of Strensham WTW in terms of quantity (Figure 4.33) and as a percentage of TTHM (Figure 4.34). After this time it shares the position with $CHBrCl_2$, where the two are seen to alternate between one having concentrations that are high when the other is low (and vice versa). Percentage shares of $CHBr_3$ (average ~ 7.5 %) and $CHBr_2Cl$ (average ~ 32.9 %) remain more stable throughout the period.

The relative quantities of chlorinated and brominated THM species formed is dependent on the ratios of chlorine to bromide, chlorine to TOC and TOC to bromide. It will also be dependent on the nature of the precursor material and the treatment to which the water is subjected. Consequently, the observed variability in raw water quality and WTW operations at Strensham WTW, will affect the above ratios, hence determining THM speciation.

Increased removal of organics through the WTW, or a relative fall in the concentration of organics in the raw water, will lead to an increase in the ratio of bromide to TOC, and a concurrent shift towards more brominated THMs. Figure 4.35 shows the concentration of raw water TOC to correlate temporally with the percentage of final water TTHM that is $CHCl_3$, with a reasonable linear relationship between the two ($R^2 \sim 0.47$, significant at the 1 % level) (Figure 4.36). The increased removal of organics across the WTW (section 4.4.1) and the move away from pre-chlorination, will have led to less organics being present at the time of chlorination giving possible explanation for the decrease in the percentage of $CHCl_3$ over the time period.

The decline in chlorine concentrations at the contact tank over the time period, or an increase in the amount of bromide in the water, will also result in a shift in the chlorine to bromide ratio, leading to a subsequent shift in the ratio of chlorinated to brominated THM species. Although hypobromous acid (HOBr) is a weaker oxidant from a thermodynamic standpoint, it is kinetically more labile than its chlorine analogue, hypochlorous acid (HOCl) (Amy *et al*., 1991; Clark & Bouton, 2001). Consequently, since bromide preferentially uses chlorine substitution sites, the formation of chlorinated species is reduced. However, if chlorine is in excess, or the amount of bromide is low, chlorinated species will be dominant. Figure 4.37 shows percentages of brominated species in final water THM to temporally follow bromide concentrations in the raw water, with a reasonable relationship observed between the two (R^2 ~ 0.71, significant at the 1 % level) (Figure 4.38).

The decline in the percentage of final water TTHM that is $CHCl_3$ and the switching between $CHCl_3$ and $CHBrCl_2$ represents the complicated story behind the changing bromide, TOC and chlorine concentrations observed. As with the relative contribution of each factor on THM formation, THM speciation is blurred by the numerous factors involved, leading to the controlled experiments and detailed, innovative analyses reported in chapter 6.

4.5 Strensham WTW to Shipston distribution system

Figure 4.39 shows average summer (start of May – end of September) THM concentrations at the WTW final water and outlets to distribution service reservoirs (DSR) in the Shipston zone distribution, between 2004 and 2008. The averages of the concentrations observed on the summer sampling days are also shown.

It can be seen that concentrations at both the final water and, in general, the distribution, fall year on year. The apparent dips in THM concentration as one moves through the distribution system are ambiguous (*e.g.* summer of 2006), and are likely to be a result of samples not being taken from the same slug of water, or to differences in the relative numbers of samples taken at each sampling point. It is possible, however, for THMs to decrease due to continued reactions within the distribution system that consume or transform them to other compounds

(Premazzi *et al*., 1997), although it is customary for THMs to increase as one moves through the system with increased contact time (section 2.10).

THM concentrations within the distribution system will vary temporally and spatially according to changes in the factors responsible for their formation and fate. The temporal variation shown in Figures 4.40 and 4.41 reflects the variations of raw water quality and treatment plant operations discussed in previous sections. The spatial variation shown will be due to the continuing reactions of the available organic material with the present halogens, and also essentially depends upon chlorine residual, temperature and physical characteristics such as residence time and flow.

Approximately half of the TTHM found at the customer tap is formed in the distribution system (Table 4.3). An appreciable amount is produced between the final water and Oversley Green BPS outlet relative to the rest of the distribution system, considering the short time the water spends in this section. This is due primarily to the reactivity of the water in the early stages and its subsequent decline as it moves through the distribution system. In the past considerable amounts of THM were also formed between Brailes DSR outlet and Little Compton DSR outlet towards the extremities of the system. This was a result of known problems of ebbing and flowing in the stretch of distribution system connecting these two service reservoirs, which were resolved in June 2007, with the amendments to operational pumps and DSR inlet control.

Temperature and TOC concentrations can be seen to remain steady as one moves through the distribution system (Figures 4.42 and 4.43 respectively). Bromide samples taken at the final

DSR outlet on the sampling days also show bromide concentrations to remain approximately the same. On the other hand, free chlorine concentrations (Figure 4.44 and 4.45) can be seen to be variable in distribution. This variability is attributable to changes to both operational practices and differences in chlorine decay. Free chlorine concentrations are noticeably lower in the summer compared to the winter as a result of operational interventions to reduce set point chlorine concentrations to combat the THM challenge. Chlorine concentrations will also dissipate more rapidly due to the higher temperatures. As a consequence of lower chlorine concentrations in the distribution system it is possible that bacterial numbers will increase, and as Chapter 7 will discuss, there is therefore a trade-off between balancing microbiological and THM compliance.

4.6 Inter-comparison of 6 WTW and parts of their distribution systems

The following section explores the differences in raw water quality, treatment processes and distribution system characteristics of the other five WTWs investigated. An attempt is made to substantiate the effects of these differences on THM formation, shown by the observed variations in THM concentrations through the WTWs and distribution systems highlighted in Figure 4.1. A summary of the primary parameters relating to THM formation at each of the six WTWs is provided in Table 4.4.

Each WTW obtains its water from either river or ground water sources, or a mixture of the two (see Table 3.1), and each has some degree of raw water storage prior to treatment proper. Differences in the storage characteristics, such as storage time and associated reservoir processes such as stratification, NOM decay by various means seasonal, will each effect DBP formation seasonally.

Raw water TOC and UV_{254} absorbance concentrations (Figures 4.46 and 4.47) show some WTWs to have relatively high organic content, Whitacre WTW (average ~ 6.55 mg/l TOC / 0.20 cm^{-1} UV_{254}), Draycote WTW (6.74 mg/l / 0.14 cm^{-1}) and Campion Hills WTW (6.44 mg/l / 0.23 cm^{-1}), in comparison to the others, Church Wilne WTW (3.51 mg/l / 0.10 cm^{-1}) and Melbourne WTW (4.32 mg/l / 0.13 cm^{-1}). The lower mean concentrations in the River Dove (Melbourne) and the River Derwent (Church Wilne) are probably due to the nature of the catchments at the southern end of the Pennines and lack of significant pollution.

Variability in the raw water TOC concentrations reflect the effect of differences in reservoir storage times on stabilising source water organic load. Draycote WTW, Church Wilne WTW and Melbourne WTW, each of which have sizeable amounts of storage (with capacities of 12 months, 20 days, and 30 days, respectively) show the least variation in TOC concentrations (with s.d. of 0.59, 0.70 and 0.47 mg/l, respectively). The higher means and peak concentrations in the other more variable WTWs probably reflect the lowland catchment influences of the Rivers Leam and Avon, and the Rivers Blythe and Bourne, along with the modest storage at Campion Hills WTW (s.d. ~ 1.41 mg/l) and Whitacre (s.d. ~ 1.10 mg/l).

Seasonal variation in organic content was observed at each of the WTWs, with TOC and UV_{254} absorbance concentrations being higher in autumn and winter compared to spring and summer months. Similar to Strensham WTW, Whitacre WTW and Campion Hills WTW raw water organics show responses to river flow that lead to high peaks in organics concentrations throughout the year. Summer peaks at Whitacre WTW may also be due to the problems it experiences with algal growth in raw water storage, possibly explaining the highest colour levels out of all the WTWs (Table 4.4). This is potentially problematic for both the water treatment process and the potential for THM formation as algae has been noted as significant precursor material to THM formation in previous studies (Wardlow *et al*., 1991; Graham *et al*., 1998).

Differences in the percentage removals of TOC and UV_{254} absorbance between the raw and final waters (Figures 4.48 and 4.49) contrast each of the works' ability and efficiency in organics removal. At the majority of the works there was an increase in percentage removed between 2003 and 2008, reflecting interventions to improve water quality. Works that were most effective at removing organics (Whitacre, Campion Hills and Church Wilne), also saw the highest removals of TOC through the works on the sampling days (Figure 4.50). Possible explanations for this include the relatively high coagulant doses (*e.g*. Whitacre WTW and Church Wilne WTW) in comparison to other works, and the application of ozone at Campion Hills WTW (section 3.3.3).

The greatest removal of TOC at each of the works occurs across the clarifiers, with between 16 and 30 % reductions in raw water TOC concentration (between 47 and 67 % of the total removed across the WTW). The degree of NOM removal by coagulation is impacted upon by many factors, such as coagulation pH, characteristics of organic and inorganic compounds, coagulant type and dose, and the plant design and operation. Variations in TOC removal across the coagulation stage will be attributable to not only changes in coagulant dose and pH, but also to the nature of the organics in the water and their applicability of removal. Draycote

WTW and Melbourne WTW showed the lowest removal of TOC across the clarifiers and the works as a whole, which could be explained by the relatively low coagulant dose at Melbourne WTW, while at Draycote WTW the reasoning is probably due to the hydrophilic organic fraction, as the coagulant dose and pH are reasonably high and low respectively, compared to the other WTWs (Table 4.4). Unlike at Melbourne, where low raw water TOC concentrations result in reasonably low final water TOC concentrations (average ~ 2.97 mg/l), high raw water concentrations at Draycote WTW mean the low removal across the WTW leaves final water TOC concentrations considerably higher than at the other WTWs Concentrations at Draycote WTW final water over 2008 ranged between 4 and 5 mg/l in comparison to the WTWs where concentrations generally ranged between 1.5 and 3 mg/l over the same time period (Figure 4.51).

The highest average bromide concentrations in the raw water were observed at the WTWs that also have the highest raw water organic concentrations. Bromide data were limited for Melbourne WTW and also for Campion Hills WTW, post-2004 (Figure 4.52), and is not routinely sampled at any point through the rest of the WTWs. Campion Hills WTW was the only one of the investigated works that receives part of its source water from groundwater (approximately 10 % of routine operational flow). Data were limited for the two borehole sources but the available data for one of the boreholes, Campion Terrace, suggest concentrations of approximately 160 µg/l.

Strensham WTW had the greatest variability in bromide concentrations due to the combination of the scale of the catchment, giving flood hydrographs in the scale of weeks rather than hours of the smaller catchments, in addition to the significant bromide inputs from parts of the West Midlands conurbation and towns upstream. Draycote WTW and Whitacre WTW have the lowest variability, the former reflects the size of the storage being consistent with surrogate organics observations, the latter being somewhat surprising at first, but probably reflects the small size of the River Bourne and River Blythe catchments leading to a flood hydrograph of a few hours and hence the probability of low bromide concentrations being rarely detected in a low frequency sampling regime. The temporal variability in the soluble carbon concentrations is consistent with the time scale of algal activity in bank-side storage facilities noted previously.

The necessary dose of chlorine to accomplish a desired objective will not only allow for the variation in water flow, but will also compensate for the variations in water quality described. Average chlorine concentrations at the pre- / post-contact tank and final water sampling points are shown in Figure 4.53. WTWs where contact tank inlet concentrations were high (Whitacre WTW, Draycote WTW and Campion Hills WTW), observed the greatest consumption of free chlorine across the contact tank. These works also had the highest average raw water TOC and bromide concentrations. Consequently, average TTHM concentrations at the contact tank outlets to Whitacre WTW (32.1 µg/l) and Draycote (26.8 µg/l) were observed to be higher in comparison to the other WTWs (average ~ 24.4 µg/l) on the sampling days. At Campion Hills WTW, THM concentrations were found to be lower at this point due to the shorter contact time, but considerable amounts of THM were formed by the final water, due to the water being stored at the end of the treatment stream in a storage reservoir for between 22 and 24 hours. With the exception of this site, between 35 and 65 % of the total THM formed by the end of the system was formed across the contact tank on the sampling days.

TTHM concentrations at each of the WTW final waters reflect the seasonal variation and also the decrease in concentrations noted at Strensham WTW (Figure 4.54). The most noticeable decrease in final water THM concentrations was observed at Church Wilne WTW, which went from having some of the highest observed concentrations in 2004 to some of the lowest observed later in the period (Figure 4.55). Possible reasons for this include the retrofit of the contact tank, which was previously known to produce 'dead spots', the slight reduction in TOC concentrations in the raw water (Figure 4.46) and the improvement in WTW treatment operations, including the introduction of additional GAC process units.

Interestingly, chloroform is only the dominant THM species at three of the investigated WTWs, somewhat contradicting the conventional view that this is the most prevalent species (section 4.5.5). This is possibly due to the increased removal of organics through each of the works and the increased influence of bromide on THM formation. Chloroform concentrations were found to be lowest at Campion Hills, with the predominance of brominated species likely to be a result of the pre- and intermediate ozone treatment process provided at this WTW.

4.7 Conclusions

A wide range of contributing factors that caused the inter-system and temporal variation in final water TTHM concentrations displayed in Figure 4.1, have been assessed in each of the studied WTWs and a segment of their associated distribution systems. Some specific conclusions regarding Strensham WTW (to which the majority of the Chapter's analysis was devoted):

- River Severn flow was shown to be a highly influential factor on the raw water quality entering the WTW. Due to the large and varied catchment of the River Severn, the influences on organic and bromide concentrations are more than natural variation, with a variety of both natural and anthropogenic source inputs experiencing peaks at different times of the year.

- Organic concentrations, represented by the surrogates TOC and UV_{254} absorbance, were found not to vary significantly seasonally (Figure 4.4). A positive relationship with river flow was observed for both (Figures 4.7 & 4.8, respectively), principally due to catchment run-off transport effects and characteristics. Organics removal through the WTW resulted in an approximate 55 % reduction of the raw water TOC and 80 % reduction of the UV_{254} absorbance concentrations, by the final water. The clarification process accounted for the majority of this decline (60-80 %). The WTW appears to be well geared to respond to changes in river water quality with changes in coagulant dose and clarification pH enabled by the online measurement of turbidity and UV_{254} absorbance concentrations. Both TOC and UV_{254} absorbance concentrations removals across the WTW were shown to be correlated to coagulant dose, with approximately 10 % and 8 % reductions of TOC and UV_{254} absorbance as a response to a 1 mg/l increase in the coagulant dose.

- Bromide was shown to be low flow critical, reflecting the dilution mechanism as key in controlling bromide concentrations in the river. Concentrations were shown not to decrease substantially through the WTW, although bromide conversion across the contact tank was more evident (Figure 4.24).

- Final water THM speciation correlated with raw water TOC and raw water bromide concentrations due to raw water quality variations and the shifting carbon : chlorine : bromide ratios in the contact tank (Figures 4.36 and 4.38).

- Temperature was shown to have a detrimental effect on chlorine consumption and THM formation. The temperature was lower in the summers of 2007 and 2008 compared to 2006 and could give a misleading interpretation of the effects of WTW interventions.

- A considerable reduction in TTHM concentrations was observed over the study period (Figure 4.27). A five-year data set showed final water THM concentrations to be correlated with final water TOC and temperature. The relationships have been quantified linearly. Little bromide data was available at this point. Unexplained variance led to the requirement for controlled experiments, conducted under both ambient and laboratory conditions, designed to simulate operational conditions.

Each of the six WTWs will have different amounts of TTHM within their final waters and distribution systems dependant on source water, treatment and supply practices. In an attempt to summarize the relative importance of each, a summary of indicative concentrations of the main contributing factors to THM formation is shown in Table 4.5 for the summers of 2007 & 2008, of which the main conclusions drawn for each of the five remaining WTWs are;

- **Whitacre WTW** - out of all the investigated WTWs, Whitacre WTW poses the greatest concern to THM formation through the works. It has some of the highest TOC and bromide concentrations in the raw water which, coupled with the high chlorine concentrations applied across the contact tank, lead to the most significant THM formation by the end of WTW treatment stream (excluding Campion Hills where there is final water storage). Due to the comparatively short distribution system, high chlorine concentrations are found through to the customer tap, but do not produce a significant amount of additional THM from that at the WTW final water due to low residence times (approximately 60 % of TTHM formed in distribution system occurs by final water). High bromide concentrations in the raw water do not appear to correspond with a high percentage of brominated species in the final water THM concentrations, with the second lowest proportion out of the six WTWs. This could possibly be a result of the high algae concentrations and / or high and variable TOC concentrations that would provide competition in both the bromide : organics ratio and organics : chlorine ratio.

- **Melbourne WTW –** through a combination of low raw water TOC and bromide concentrations, and low chlorine dosages, this WTW observes low THM concentrations at the final water sampling point. However, due to it having the longest retention times in the distribution system, coupled with the relatively high chlorine concentrations at selected points, large amounts of THM are formed (approximately 60 % of total formed) and low chlorine concentrations are observed at the extremities of the distribution system.

- **Draycote WTW –** this WTW observes the most stable raw water quality, particularly in terms of organics, attributable to the longest raw water storage time of the WTWs. Bromide concentrations in the raw water have fallen in recent years from the noted problem concentrations observed previously in the source rivers (Smith, 2005). The fall in TOC concentrations across the WTW is the lowest out of each of the WTWs indicating a difficult to remove fraction of the relatively hydrophilic organic matrix. THM concentrations at the final water are roughly average in comparison to the other WTWs, but the high TOC concentrations in the final water could be the reason why the majority of THM is formed in the distribution system (approximately 60 % of total formed).

- **Campion Hills WTW –** although this WTW exhibits the lowest THM concentrations at the end of the treatment stream, by the time the water enters into distribution it has some of the highest due to a final water storage reservoir that has a residence time of up to 22 hours. Although formation of THM through the WTW is low, due to the chlorination age of the water there are plenty of suitable reactants present in the water to form THMs in the final water storage reservoir, where chlorine concentrations remain high. The high percentage of brominated species at the WTW final water are caused by the use of ozone treatment (the only one of the investigated WTWs to use it) and 10 % of the raw water comes from groundwater sources (where the limited STW data suggest bromide concentrations to be high). Chlorine concentrations are high in the distribution system (*e.g.* 0.31 mg/l average at the final DSR) but due to the majority of the quick reactions taking place in the storage reservoir on site, the long retention time in the distribution system is not reflected in any significant increases in THM concentrations.

- **Church Wilne WTW –** raw water TOC and bromide concentrations are the lowest at this WTW, which is surprising given the industrial / urban mixture of land use upstream of the raw water abstraction. Low final water TTHM concentrations reflect this. However, this has not always been the case, as this WTW exhibited some of the highest final water THM concentrations in the early part of the observation period. The significant improvement in reducing THM concentrations during this period are due to noted WTW treatment improvements. Consideration of THM formation towards the extremities of the distribution system is difficult due to the lack of sampling points that are fed by water solely from the WTW, due to the mixing with a variety of waters at different ratios under different operational conditions. THM concentrations in the early stages of the distribution system where water solely from Church Wilne WTW could be sampled were, however, relatively low.

Parameter	**Sample point(s)**	**Total number in typical sampling program**
TOC	Raw water, post-clarified, post-RGF, post-GAC, post-CT, final water, final DSR outlet.	7
Bromide	Raw water, post-GAC, final water, final DSR outlet, bulk decay experiments - 12 in total (see below).	19
THM	Post-CT, final water, every available inlet / outlet to each DSR in distribution (assume average of 5 available sampling points), bulk decay experiments - 24 in total (see below).	32
Free chlorine	Pre-CT, post-CT, post-CT (de-Cl), final water, every available inlet / outlet to each DSR in distribution, bulk decay experiments - 33 in total (see below).	43 (+ duplicates)
Total chlorine	Pre-CT, post-CT, post-CT (de-Cl), final water, every available inlet / outlet to each DSR in distribution, bulk decay experiments - 31 in total (see below).	39 (+ duplicates)
R.W. bulk decay (2 hrs with THM / Br at end of test)	Raw water (initial concentration - 1.7 mg/l); 1 test over 2 hrs; 8 free Cl, 8 total Cl + 1 THM / Br at end of test.	1
F.W. bulk decay (24 hrs with THM / Br)	1 test over 24 hrs; 8 free Cl, 8 total Cl, 5 THM, 1 Br at end of test.	1
CT simulation bulk decay (4 hrs with THM / Br) on	1 test over 4 hrs based on ambient conditions on sampling day; 9 free Cl, 9 total Cl, 5 THM, 5 Br.	1

post-GAC water		
CT variation bulk decay (varying C_0, TOC and initial temp.) on post-GAC water	7 bulk decay tests (varying initial Cl, TOC and temp) over 2 hours for comparison with above bulk decay experiments. For each experiment: 8 free Cl, 8 total Cl and 1 THM / 1 Br at 2 hours.	7
pH	Raw water, pre-CT, final water.	3
Temperature	Raw water, post-GAC, final water, final DSR outlet.	4
UV_{254}	All available sampling points through WTW logged on STW databases.	Variable
Colour		Variable
Turbidity		Variable

Table 4.1; Typical samples taken on a routine sampling program at a WTW and its respective distribution system.

		Summer (June – August)			**Annual (January – December)**		
		Mean temp.	**Actual sunshine**	**Actual rainfall**	**Mean temp.**	**Actual sunshine**	**Actual rainfall**
		(ºC)	Hours	mm	(ºC)	Hours	mm
2002	*Midlands*	15.5	483.9	203.4	10.2	1403.2	926.7
	England	15.5	494	205.2	10.3	1441.3	1006
2003	*Midlands*	16.9	572	147.5	10.1	1685.2	613.8
	England	16.9	602.8	150.9	10.3	1746.9	675.4
2004	*Midlands*	16	525.4	267.9	10.2	1431.6	842.2

	England	16	544.4	270.5	10.3	1488.6	891.3
2005	*Midlands*	15.9	572.2	170	10.1	1506.6	685.4
	England	15.9	583.3	174.8	10.2	1545.9	746.7
2006	*Midlands*	17.2	654	153	10.5	1579.7	797.5
	England	17.0	676	154	10.6	1626.1	846.5
2007	*Midlands*	15.1	526	346	10.2	1556.5	930.3
	England	15.1	530	325	10.4	1590.1	943.1
2008	*Midlands*	15.4	499.9	255	-	-	-
	England	15.4	520.1	268.8	-	-	-

Table 4.2; Annual and summer temperature (ºC), sunshine (hours) and rainfall (mm) for the Midlands region and England between 2002 and 2008 (www.metoffice.co.uk).

Year	**Whitacre WTW**		**Melbourne WTW**		**Draycote WTW**		**Campion Hills WTW**		**Church Wilne WTW**		**Strensham WTW**	
	WTW	DS	WTW	DS	WTW	DS	WTW	DS	WTW	DS	WTW	DS
2003	68	32	52	48	47	53	22 (n/a)	78	n/a	n/a	n/a	n/a
2004	57	43	49	51	41	59	86 (n/a)	14	55	45	50	50
2005	35	65	43	57	43	57	n/a	n/a	51	49	41	59
2006	55	45	28	72	35	65	57 (31)	43	60	40	48	52

2007	51	49	35	65	32	68	66 (29)	34	28	72	33	67
2008	49	51	60	36	40	60	66 (31)	34	55	45	28	72
Mean	***53***	***47***	***45***	***55***	***39***	***61***	***60***	***40***	***50***	***50***	***40***	***60***

Table 4.3; Percentages of TTHM formed through the entire distribution system at the WTW (final water sampling point). Bracket values at Campion Hills indicate percentage formed by treated water sampling point (pre-FWSR). (n/a ~ data not available / limited in distribution system).

		WHITACRE		**MELBOURNE**		**DRAYCOTE**		**CAMPION HILLS**		**CHURCH WILNE**		**STRENSHAM**	
Parameter	**Location**	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*
Free Cl (mg/l)	**Pre-CT**	**1.95**	0.07	**1.32**	0.09	**1.67**	0.08	**1.70**	0.14	**1.47**	0.12	**2.11**	0.31
	Post-CT	**1.52**	0.07	**1.04**	0.07	**1.24**	0.11	**1.23**	0.09	**1.16**	0.07	**1.80**	0.35
	F.W	**0.51**	0.03	**0.42**	0.04	**0.57**	0.06	**0.48**	0.07	**0.51**	0.05	**0.49**	0.12
	Final D.S DSR / customer tap	**0.09**	0.07	**0.16**	0.08	**0.11**	0.09	**0.31**	0.07	**0.18**	0.09	**0.16**	0.09
TTHM (ug/l) 2003 – 2008 (all data)	**F.W**	**34.3**	10.2	**24.7**	6.0	**29.6**	7.9	**33.5**	8.5	**39.9**	17.5	**29.1**	11.8
	Final D.S DSR / customer tap	**64.0**	12.6	**57.3**	15.65	**64.5**	12.4	**56.3**	10.5	**54.5**	19.4	**61.1**	18.5
TTHM (ug/l) 2003 – 2008 (summer data only – May to Sept)	**Post-CT (sampling days)**	**32.1**	4.3	**19.3**	5.4	**26.8**	4.6	**16.2**	2.44	**24.6**	1.9	**26.7**	4.25
	F.W	**36.8**	10.9	**26.8**	7.9	**32.4**	7.9	**37.5**	4.5	**38.7**	15.1	**35.3**	11.4
	Final D.S	**68.9**	12.7	**64.5**	18.4	**67.2**	11.8	**61.9**	7.9	**58.3**	17.6	**70.9**	16.6

		WHITACRE		**MELBOURNE**		**DRAYCOTE**		**CAMPION HILLS**		**CHURCH WILNE**		**STRENSHAM**	
Parameter	**Location**	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*
	DSR / customer tap												
TOC (mg/l)	**R.W**	**6.55**	1.10	**4.32**	0.47	**6.74**	0.59	**6.44**	1.41	**3.51**	0.70	**5.44**	1.84
	F.W	**2.88**	0.62	**2.97**	0.36	**4.41**	0.50	**2.99**	0.54	**2.08**	0.41	**2.25**	0.38
Bromide (µg/l)	**R.W**	**115.8**	17.9	**74.2**	6.5	**93.8**	15.9	**102.6**	19.2	**81.1**	25.9	**76.2**	27.8
	F.W	**12.6**	6.47	**13.0**	7.6	**52.4**	18.0	**N/A**	N/A	**22.1**	16.0	**23.3**	7.9
UV 254 abs. (cm-1)	**R.W**	**0.20**	0.07	**0.13**	0.04	**0.14**	0.03	**0.23**	0.11	**0.10**	0.02	**0.24**	0.16
	F.W	**0.05**	0.01	**0.06**	0.01	**0.06**	0.01	**0.04**	0.01	**0.03**	0.01	**0.04**	0.02
Turbidity (F.T.U)	**R.W**	**8.25**	7.43	**1.32**	1.26	**1.01**	0.72	**11.27**	6.69	**1.74**	1.76	**12.3**	7.1
	F.W	**0.08**	0.04	**0.07**	0.04	**0.06**	0.02	**0.06**	0.05	**0.07**	0.04	**0.06**	0.03
Colour (F-Hazens)	**R.W**	**17.24**	5.35	**12.01**	3.51	**8.79**	2.14	**14.72**	6.70	**10.69**	4.46	**22.8**	14.4
	F.W	**1.04**	0.69	**1.66**	0.96	**1.33**	0.74	**0.72**	0.48	**0.88**	0.54	**0.82**	0.52
pH	**R.W**	**7.85**	0.42	**8.01**	0.31	**8.20**	0.25	**8.05**	0.26	**7.81**	0.34	**7.71**	0.31
	F.W	**7.29**	0.15	**7.62**	0.18	**7.52**	0.25	**7.53**	0.16	**7.52**	0.21	**7.56**	0.19
% reduction	**Across**	**55**	8.3	**37**	5.1	**34**	6.9	**53**	8.7	**71**	6.0	**55**	10.5

		WHITACRE		**MELBOURNE**		**DRAYCOTE**		**CAMPION HILLS**		**CHURCH WILNE**		**STRENSHAM**	
Parameter	**Location**	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*	***Mean***	*S.D*
in R.W. TOC to F.W	**WTW**												
% reduction in R.W. UV 254 to F.W	**Across WTW**	**78**	6.7	**59**	5.9	**56**	11.5	**82**	6.2	**42**	5.9	**82**	8.5
Coagulant type	**Clarifiers**	Ferripol Xl (Ferric sulphate)		Ferripol Xl		Ferric sulphate		Ferric chloride		Ferric sulphate		Aluminum sulphate / Ferripol	
Coagulant dose	**Clarifiers**	Generally between: **8.5 – 11** mg/l Fe		Generally between: **5 - 7** mg/l Fe		Generally between: **7 – 8.3** mg/l Fe		Generally between: **4 - 12** mg/l Fe.		Generally between: **7 – 10** mg/l Fe.		Generally between: **3 – 6** mg/l Fe.	
Clarification process	**Clarifiers**	HBC		DAF		DAF		HBC		HBC (x16) / DAF (x5)		HBC	
Flow	**F.W**	Generally between: **32 – 40** Ml/d		Generally between: **170 – 200** Ml/d		Generally between: **20 – 30** Ml/d		Generally between: **18 – 20** Ml/d		Generally between: **100 – 110** Ml/d		Generally between: **140 – 160** Ml/d	

Table 4.4; Average, standard deviation (S.D) and range of concentrations of various parameters through Whitacre, Melbourne, Draycote, Campion Hills, Church Wilne and Strensham WTWs between 2003 – 2008 (unless stated).

Key (Table 4.4);

F.W. - Final water
R.W. - Raw water
Pre-CT - Pre-contact tank
Post-CT - Post-contact tank
D.S. - Distribution system
DSR - Distribution service reservoir
HBC - Hopper bottom clarifiers
DAF - Dissolved air flotation

	Whitacre	**Melbourne**	**Draycote**	**Campion Hills**	**Church Wilne**	**Strensham**
	Indicative concentrations during 2007 / 2008 summer periods					
	Water Treatment Works (WTW)					
Raw water bromide conc. (µg/l)	🟥 **120 - 130**	🟩 **60 - 70**	🟧 **80 - 90**	🟥 **100 - 110**	🟧 **75 - 85**	🟩 **70 – 80**
Raw water TOC conc. (mg/l)	🟥 **6.5**	🟧 **4.5**	🟥 **6.5**	🟥 **6**	🟩 **3**	🟥 **6**
Final water TOC conc. (mg/l)	🟧 **2.75**	🟧 **3**	🟥 **4.5**	🟧 **3**	🟩 **1.75**	🟩 **2.25**
Contact tank inlet free chlorine conc. (mg/l)	🟥 **1.95**	🟩 **1.35**	🟧 **1.65**	🟧 **1.7**	🟧 **1.5**	🟥 **1.95**
Contact tank outlet free chlorine conc. (mg/l)	🟥 **1.55**	🟩 **1.05**	🟧 **1.20**	🟧 **1.25**	🟧 **1.15**	🟥 **1.55**
% of final water THM that are brominated species	🟧 **60**	🟧 **65**	🟧 **68**	🟥 **85**	🟧 **73**	🟩 **55**
Final water THM conc. (µg/l)	🟥 **30 – 40**	🟧 **20 – 30**	🟧 **20 – 30**	🟥 **30 – 40**	🟧 **20 – 30**	🟧 **20 – 30**
	Distribution system (DS)					
Approx. travel time to extremities of system (hrs)	🟩 **40-60**	🟥 **140 - 165**	🟧 **60 - 80**	🟥 **100 - 120**	**?**	🟥 **90 - 120**
Free chlorine range (mg/l) (not incl. final water)	🟥 **0.15 – 0.45**	🟥 **0.05 – 0.45**	🟥 **0.1 – 0.4**	🟥 **0.15 – 0.4**	🟩 **0.05 – 0.3**	🟧 **0.05 – 0.35**
TTHM high range (mg/l)	🟥 **60 – 70**	🟥 **55 – 65**	🟥 **55 – 70**	🟧 **50 – 60**	🟩 **40 – 50**	🟧 **50 - 60**
Percentage of THM formed in WTW / DS	**60 / 40**	**40 / 60**	**40 / 60**	**65 / 35**	**?**	**45 / 55**

Table 4.5; Indicative concentrations of select water quality parameters during the summer of 2007 / 2008, which influence THM formation in the WTW and distribution system. **GREEN - Low risk to THM formation, ORANGE - Medium risk to THM formation, RED - High risk to THM formation.**

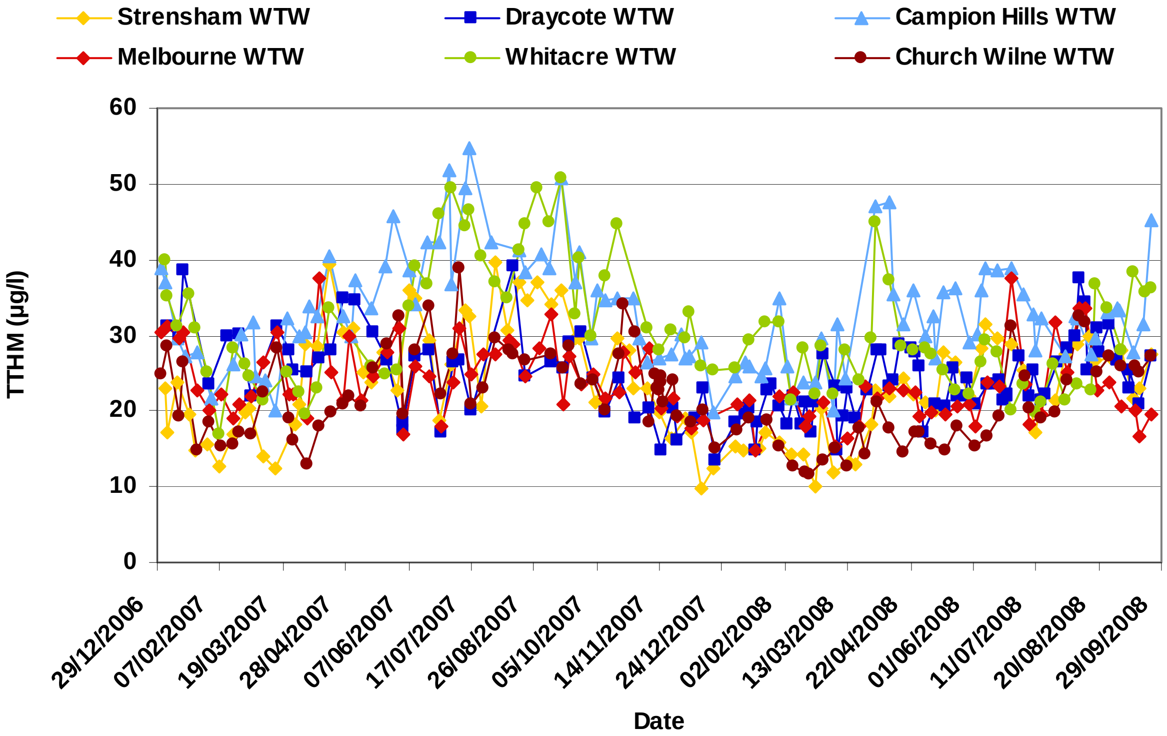


Figure 4.1; Temporal variability in TTHM concentrations at each of the six WTWs between the start of 2007 – end of September 2008.

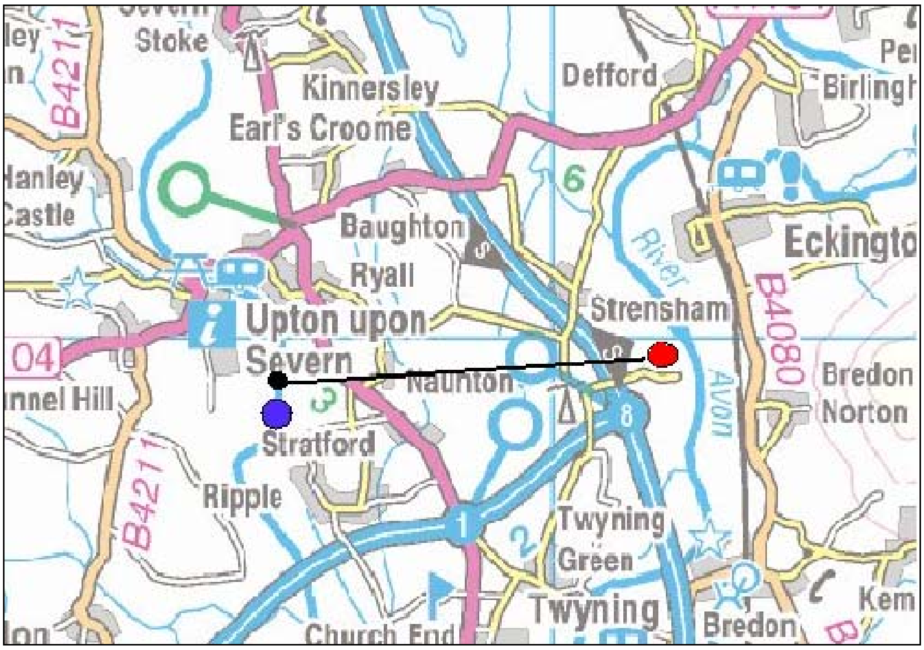


Figure 4.2; Location of Strensham WTW (red dot) and river abstraction point (black dot) in relation to Saxons Lode flow measurement station (blue dot) (Environment Agency website, 2009).

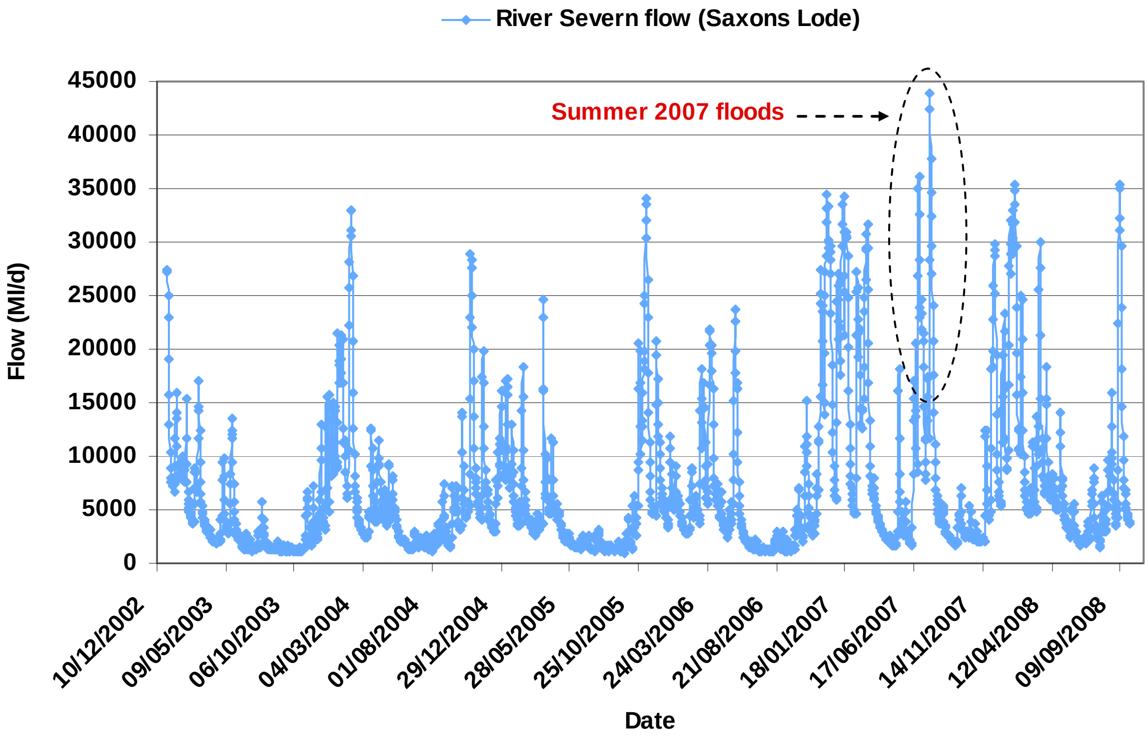


Figure 4.3 ; River Severn flow data (from Environment Agency) - based on daily averages at Saxon's Lode measurement station.

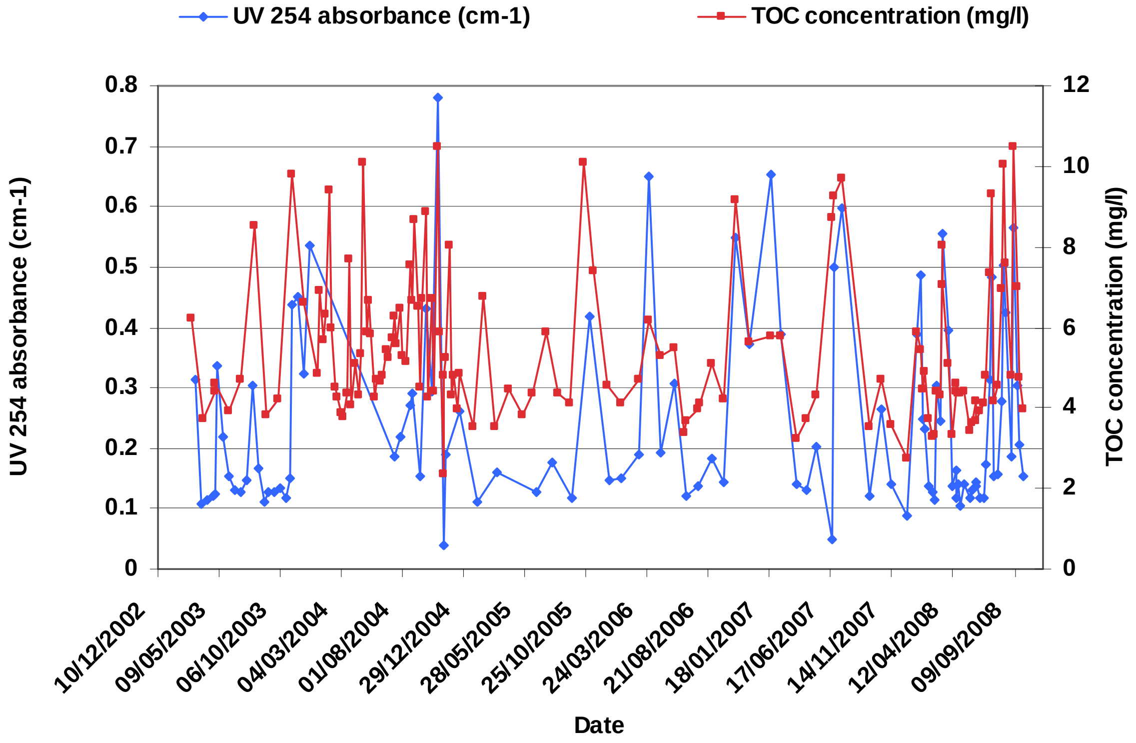


Figure 4.4; Raw water TOC and UV_{254} absorbance at Strensham WTW between 2003 and 2008.

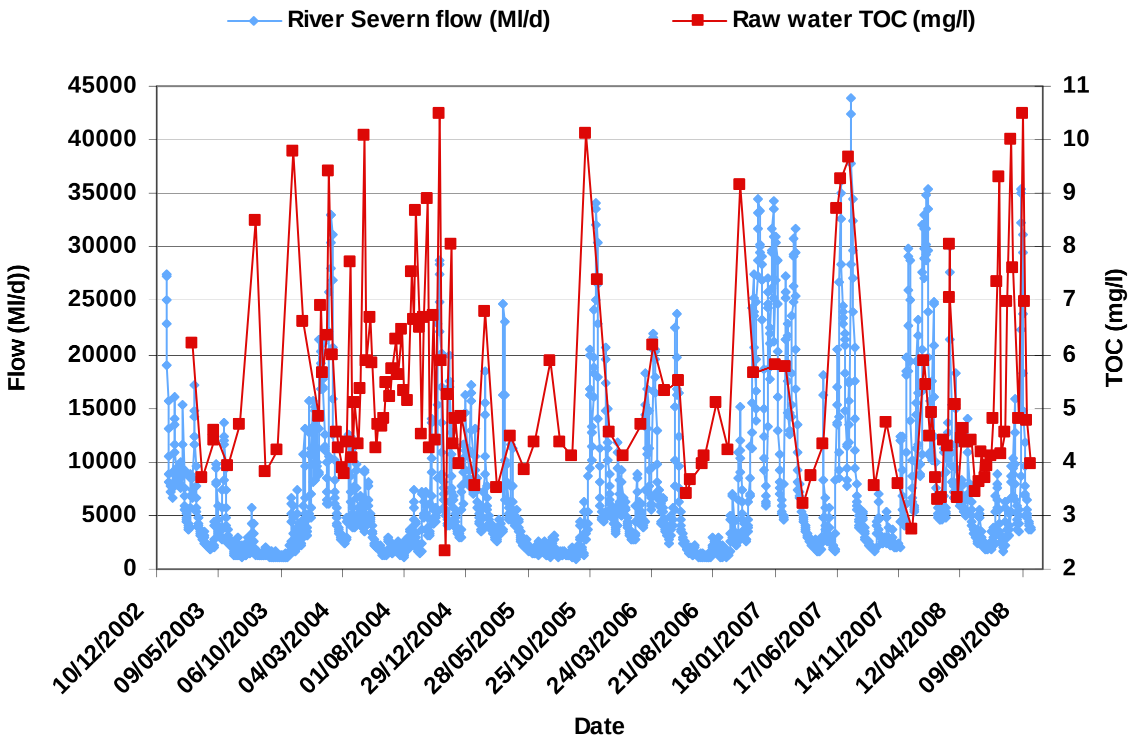
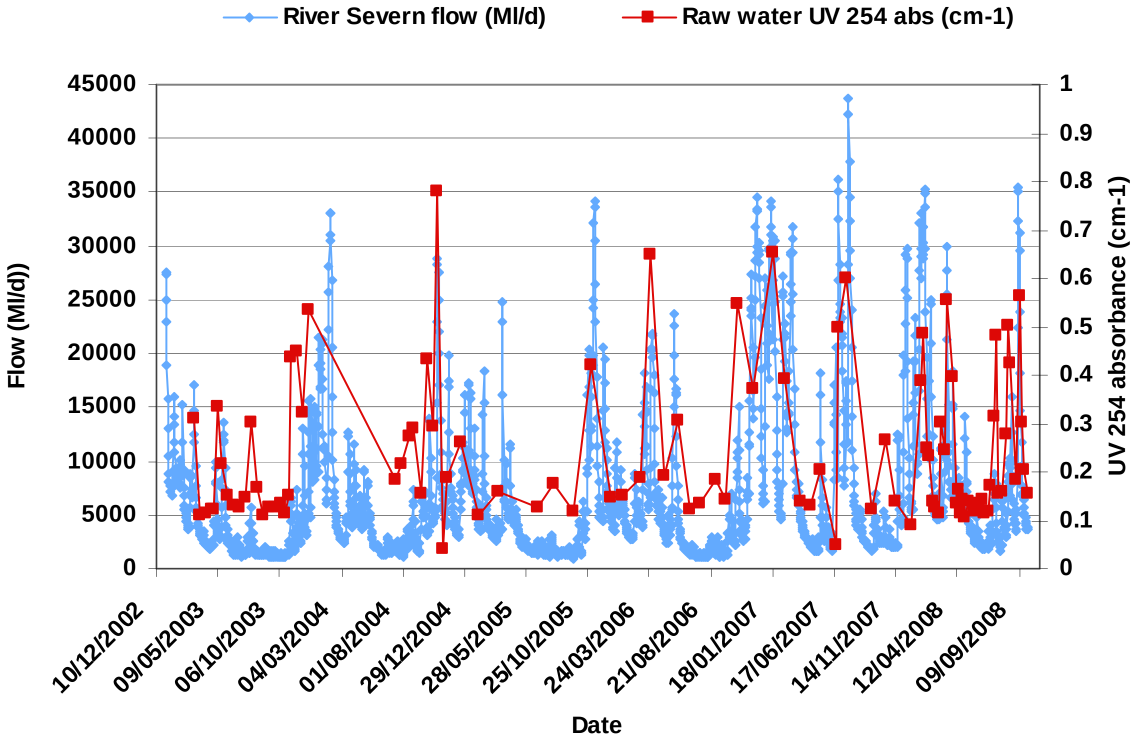


Figure 4.5; River Severn flow data (from Saxons Lode measuring station) with TOC concentrations in the raw water entering Strensham WTW.



Figrue 4.6; River Severn flow data (from Saxons Lode measuring station) with UV_{254} absorbance in the raw water entering Strensham WTW.

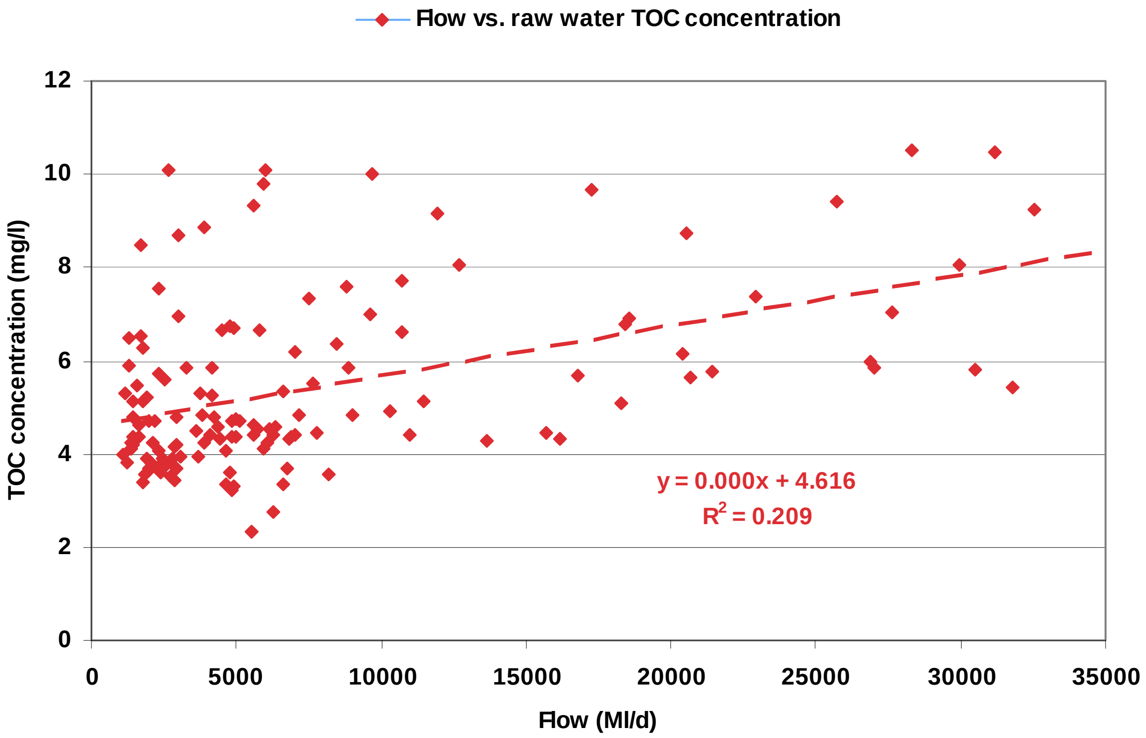


Figure 4.7; River Severn flow versus raw water TOC concentration entering Strensham WTW between 2003 – 8 (X-Y scatter plot with linear trend line).

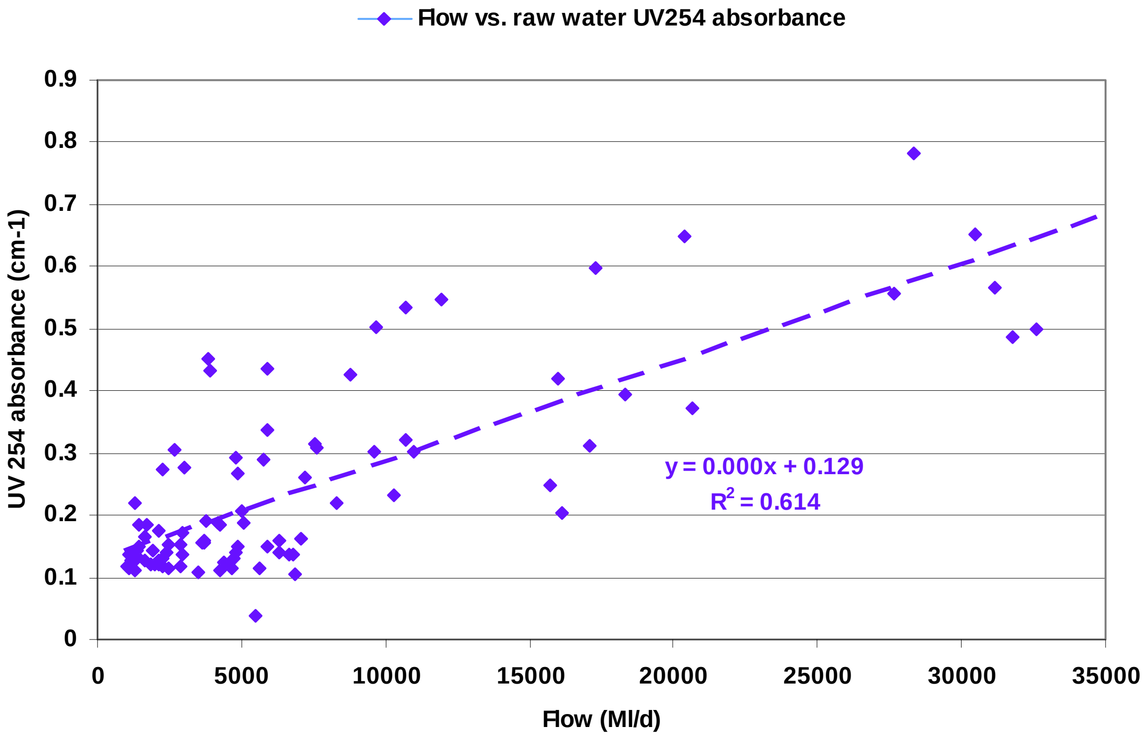


Figure 4.8; River Severn flow versus raw water UV_{254} absorbance entering Strensham WTW between 2003 – 8 (X-Y scatter plot with linear trend line).

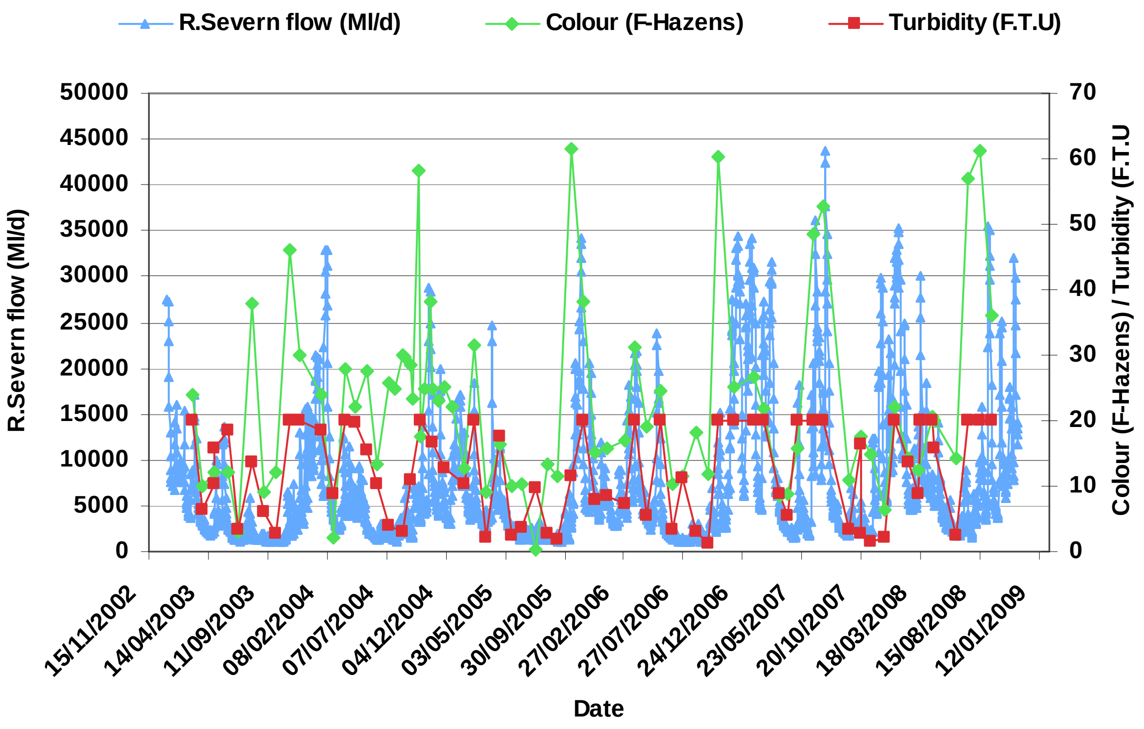


Figure 4.9; River Severn flow and Strensham WTW raw water colour and turbidity levels between 2003 and 2008.

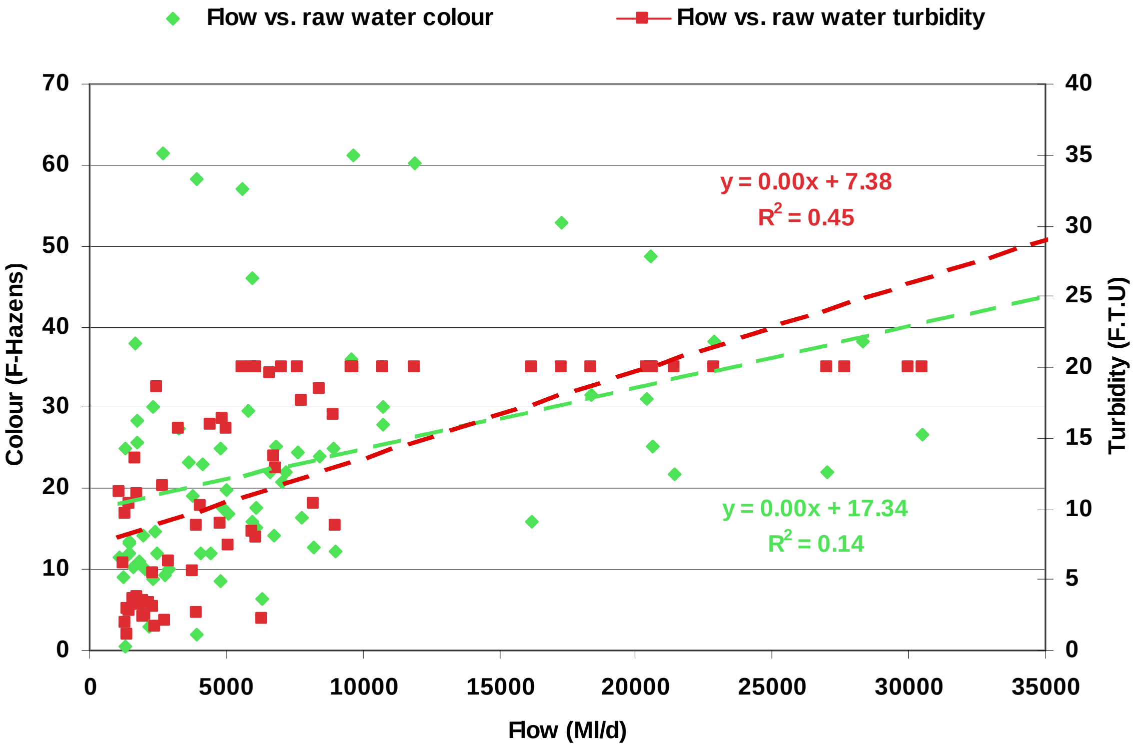


Figure 4.10; X-Y scatter plot showing relationship between flow / turbidity, and flow / colour, 2003 – 2008 data.

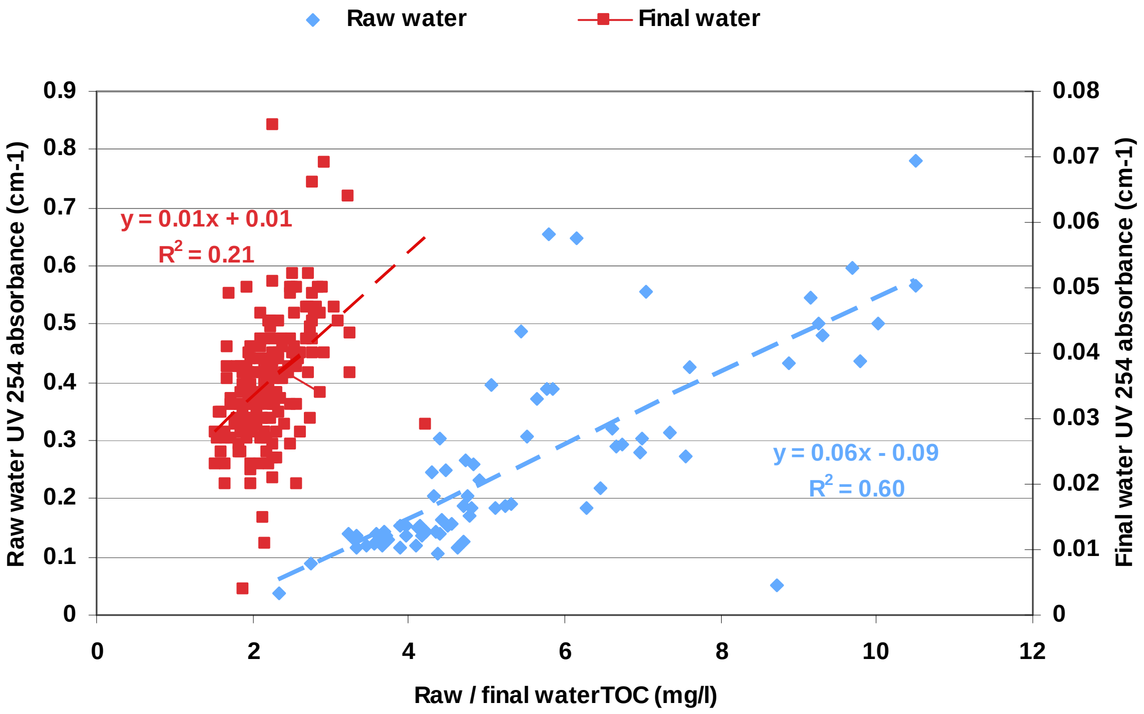


Figure 4.11; X-Y scatter plots of raw water UV$_{254}$ absorbance versus TOC (L.H.S. axis) and final water UV$_{254}$ absorbance versus TOC (R.H.S. axis).

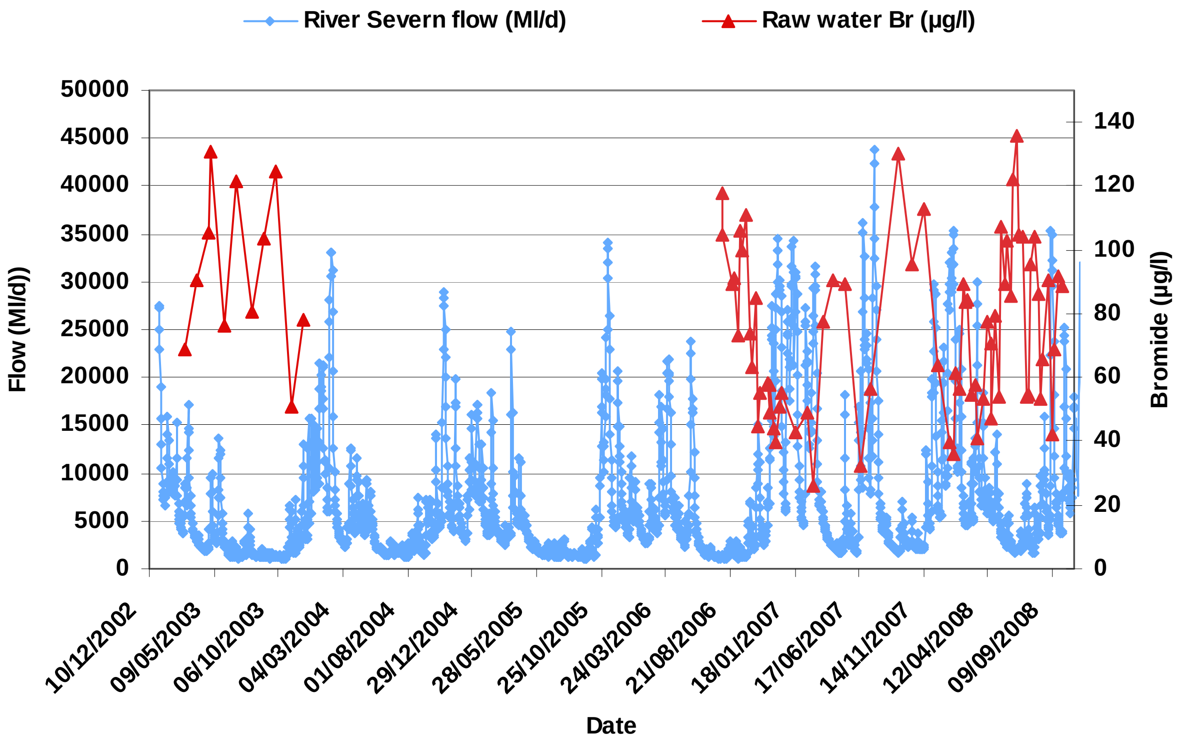


Figure 4.12; River Severn flow with bromide concentrations in the raw water entering Strensham WTW.

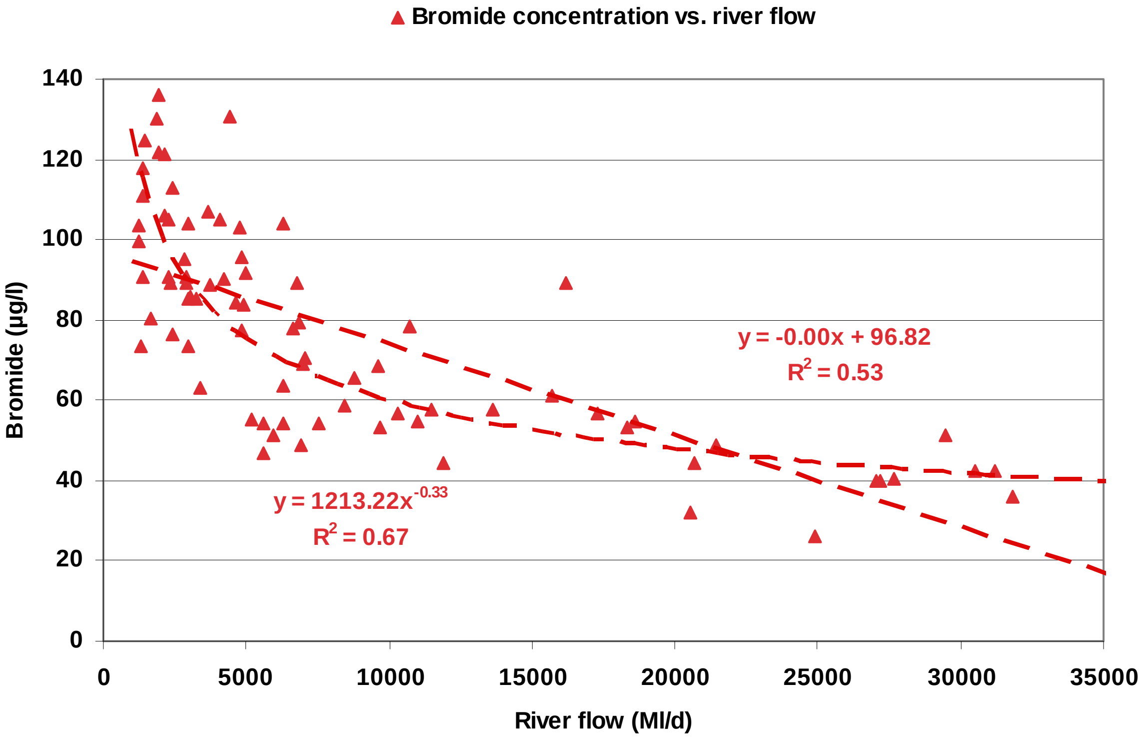


Figure 4.13; River Severn flow versus raw water bromide concentration entering Strensham WTW between 2003 – 8 (X-Y scatter plot with linear (dashed) and power relationship trend lines).

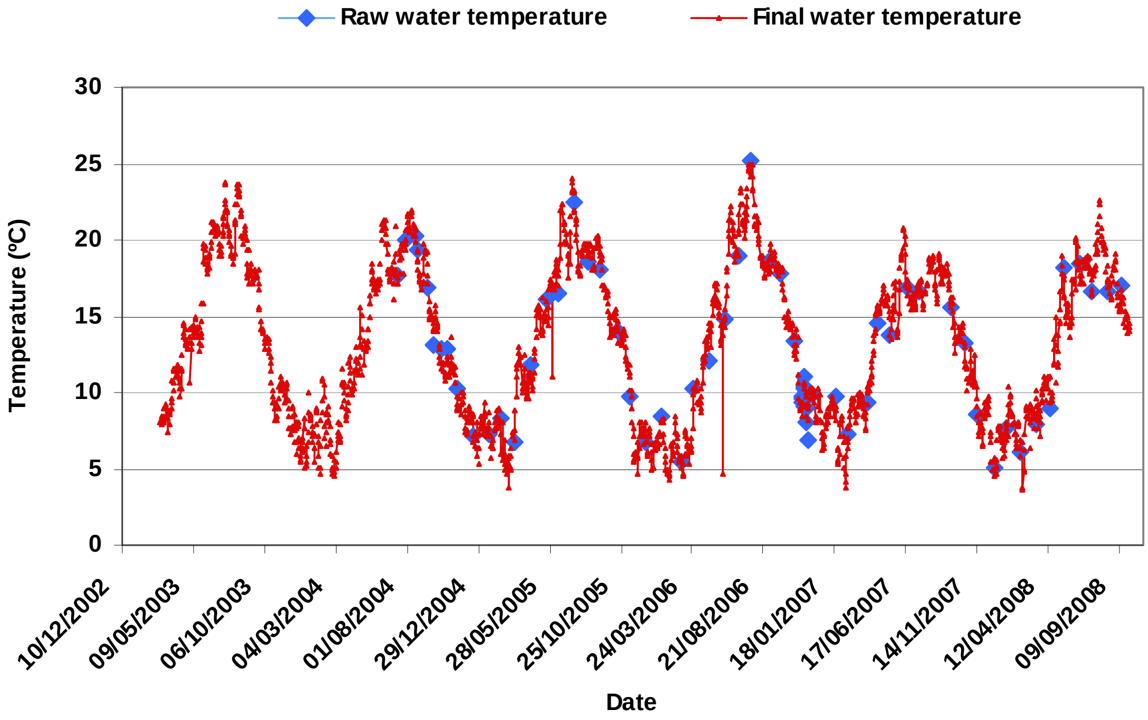


Figure 4.14; Temperature at the raw and final water sampling points at Strensham WTW.

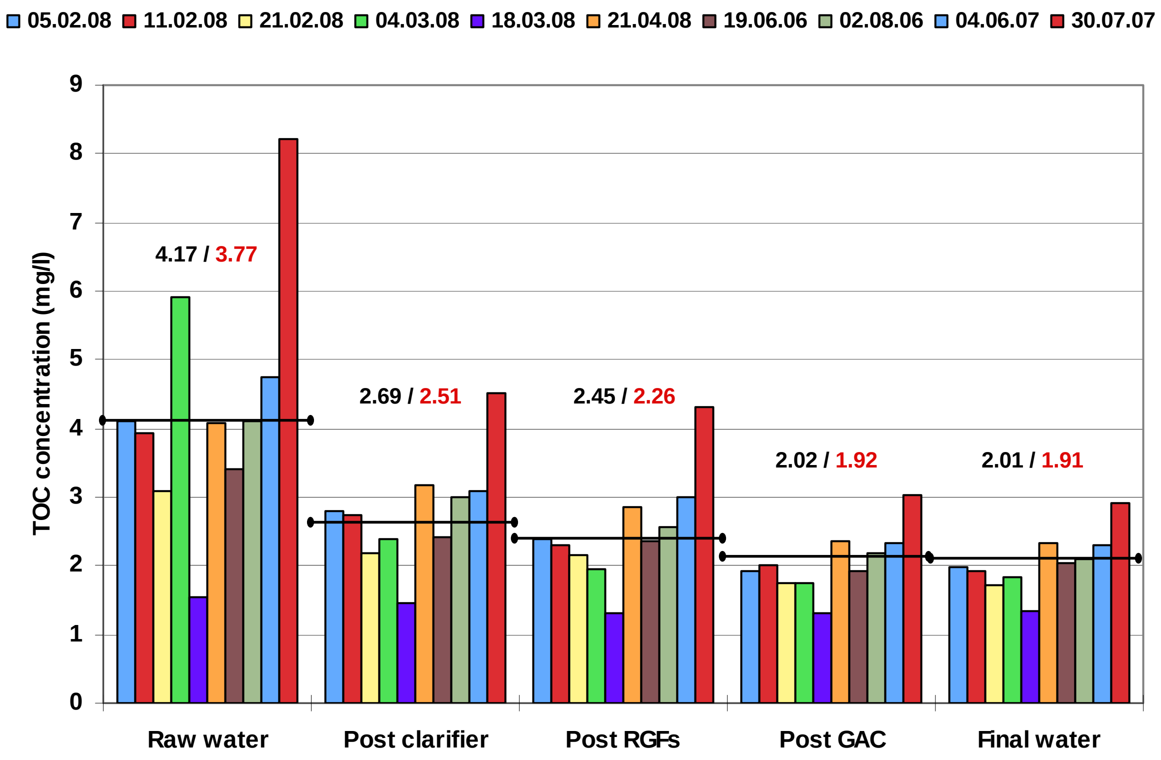


Figure 4.15; TOC concentrations through Strensham WTW on sampling days. Averages in black for all sampling days. Excluding the high concentrations measured on 30.07.07 (in red).

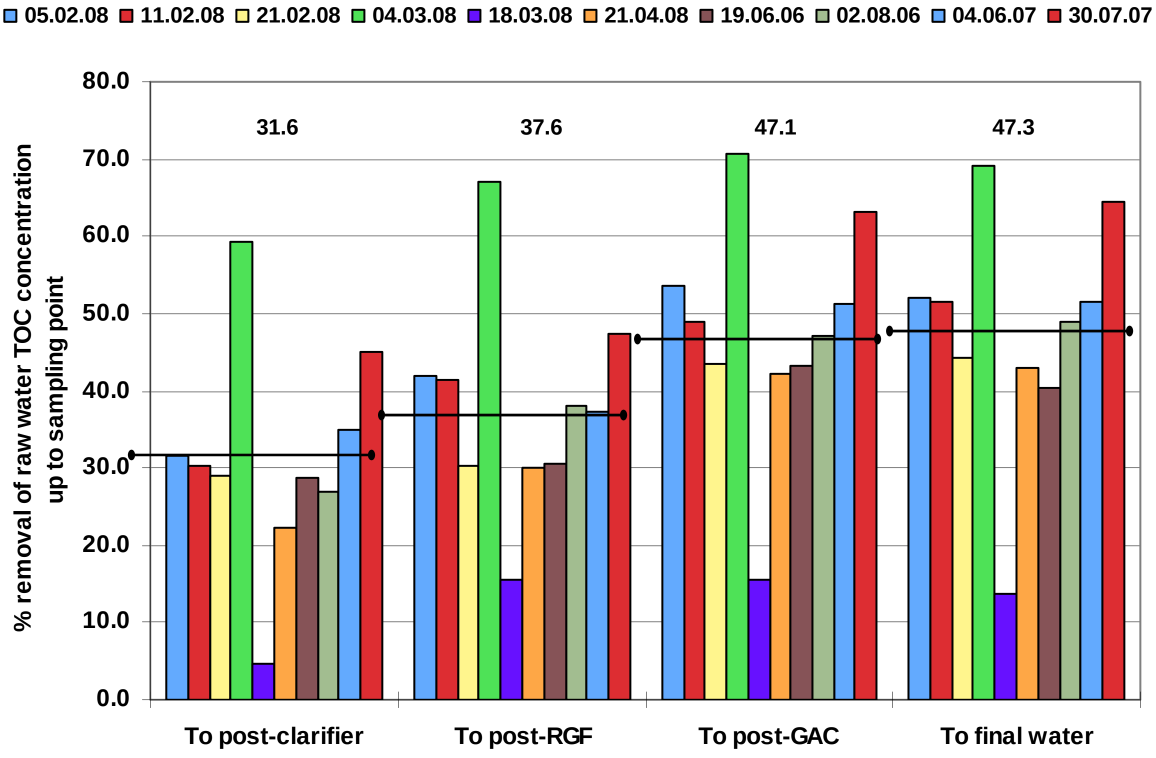


Figure 4.16; Percentage removals of raw water TOC concentrations to selected points (x-axis) from samples taken at Strensham WTW.

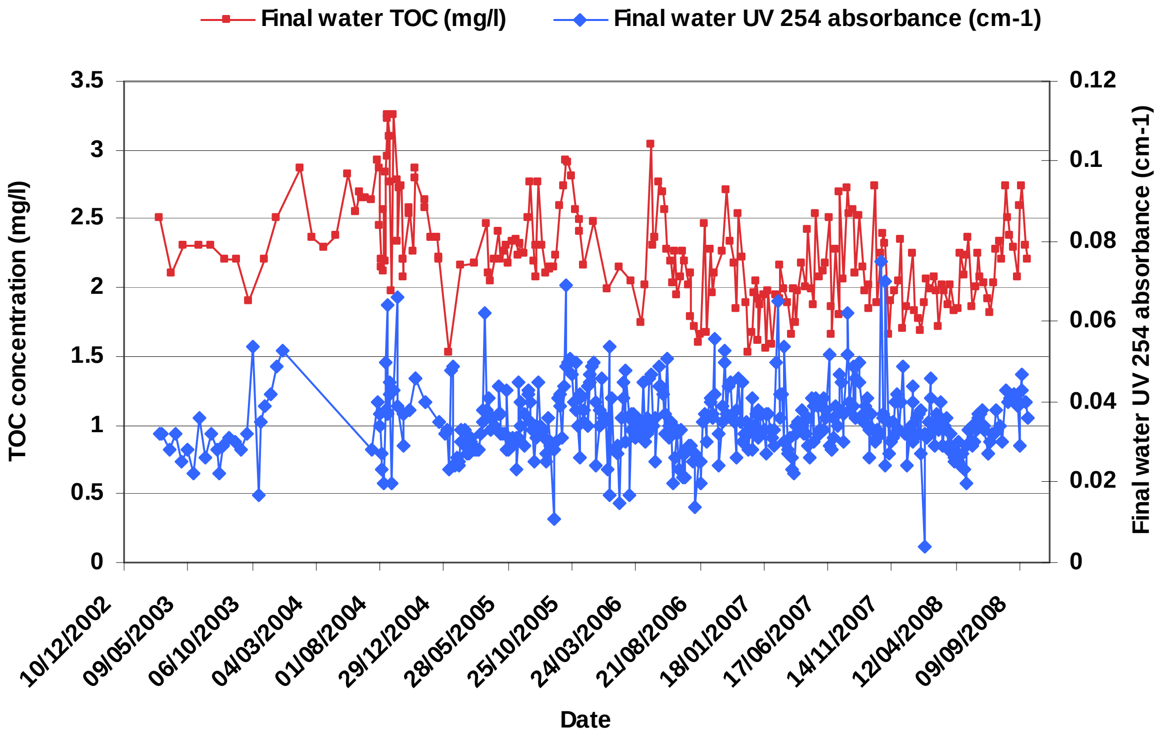


Figure 4.17; Final water TOC and UV$_{254}$ absorbance concentrations between 2003 – 2008.

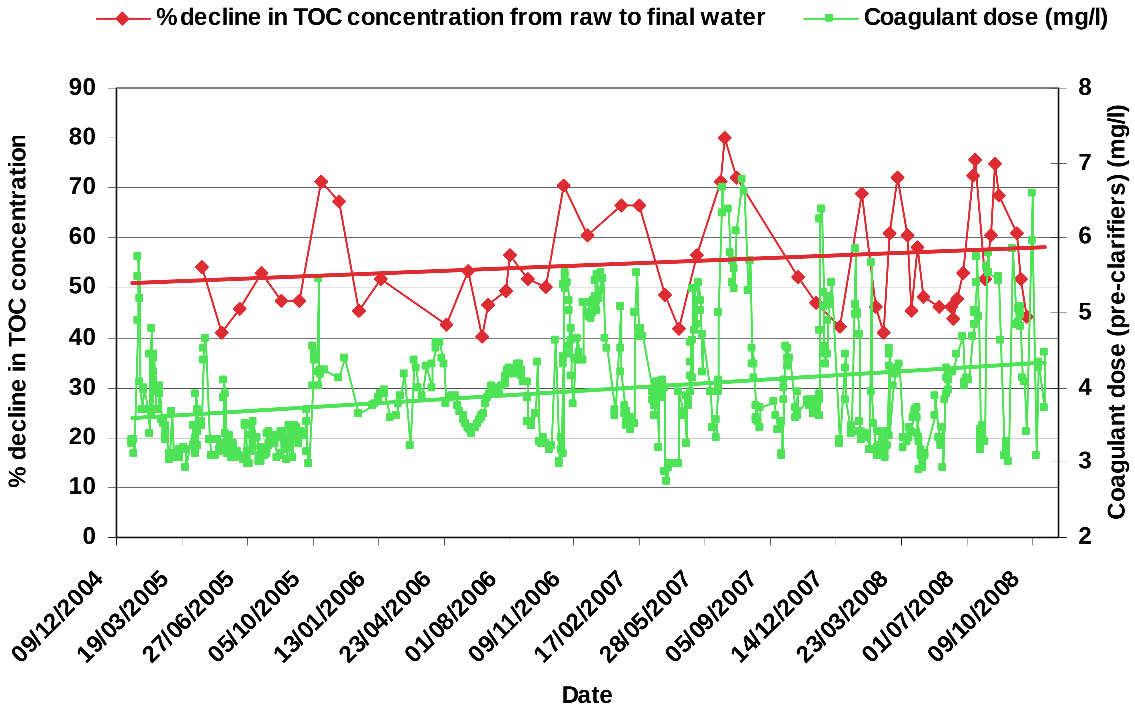


Figure 4.18; Percentage decline in raw water TOC concentrations to final water at Strensham WTW and coagulant dose at pre-clarifier stage, between 2005 – end September 2008 (limited to when TOC samples taken at raw and final waters on same day).

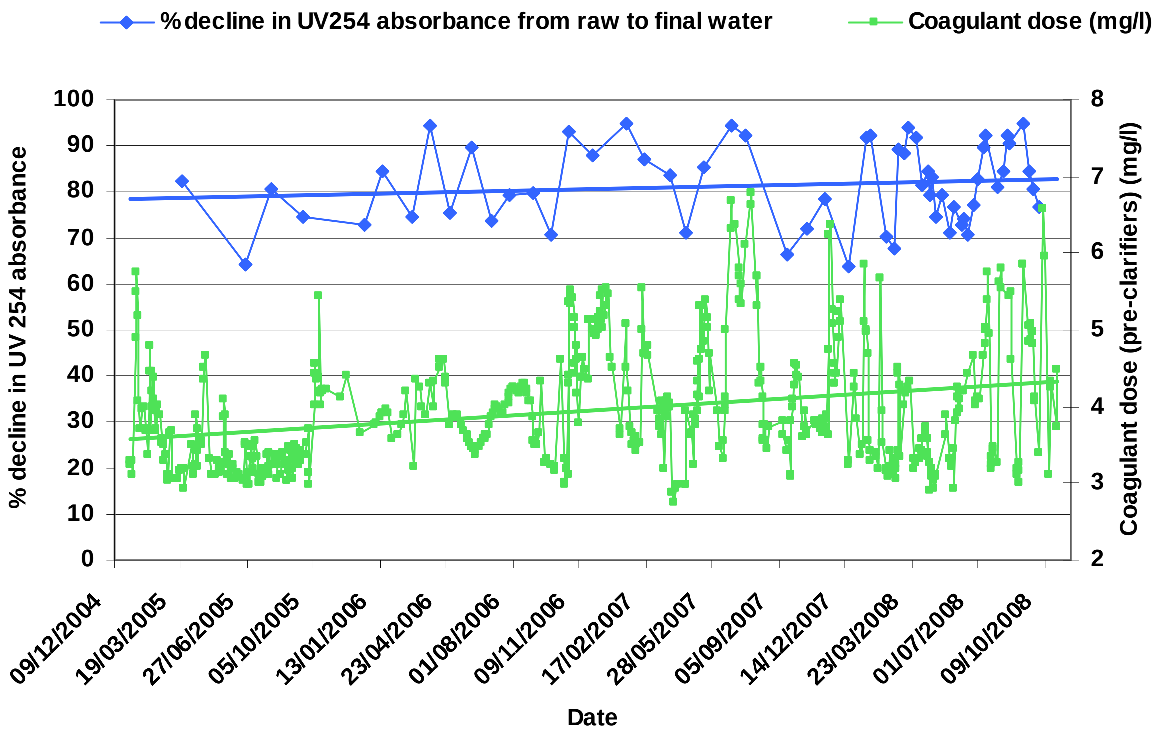


Figure 4.19; Percentage decline in raw water UV_{254} absorbance to final water at Strensham WTW and coagulant dose at pre-clarifier stage, between 2005 – end September 2008 (limited to when TOC samples taken at raw and final waters on same day).

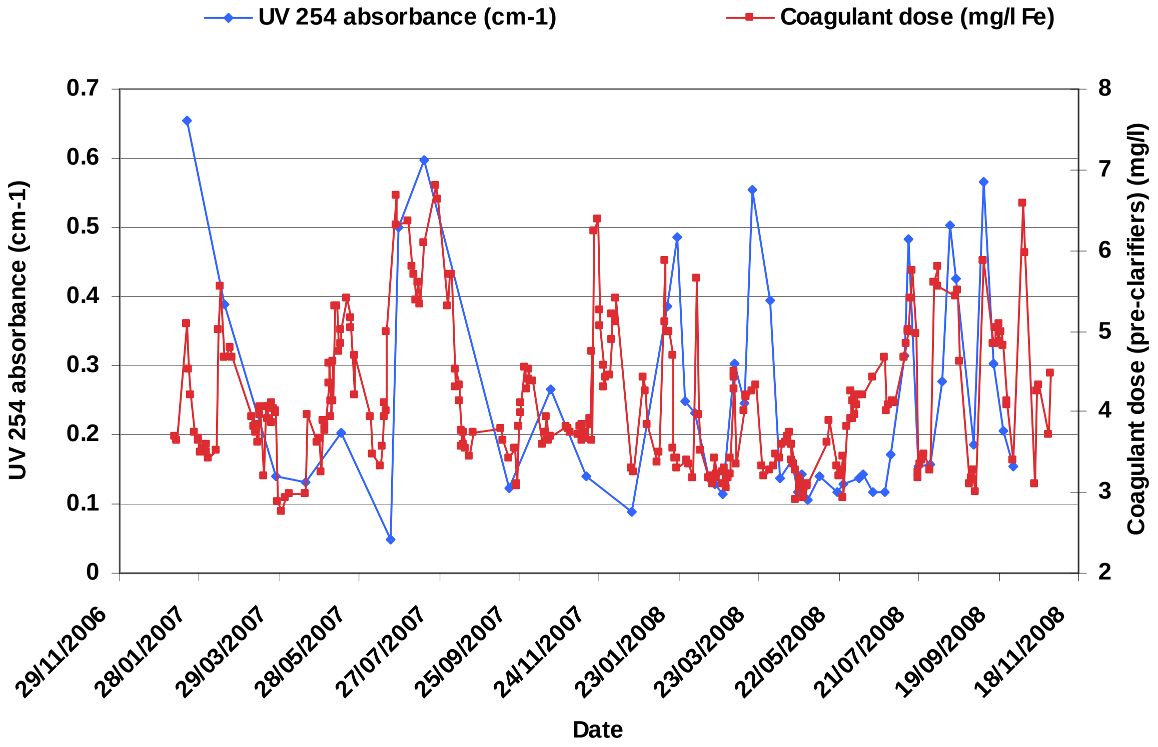


Figure 4.20; Raw water UV_{254} absorbance and coagulant dose at the pre-clarifier stage between 2007 and 2008.

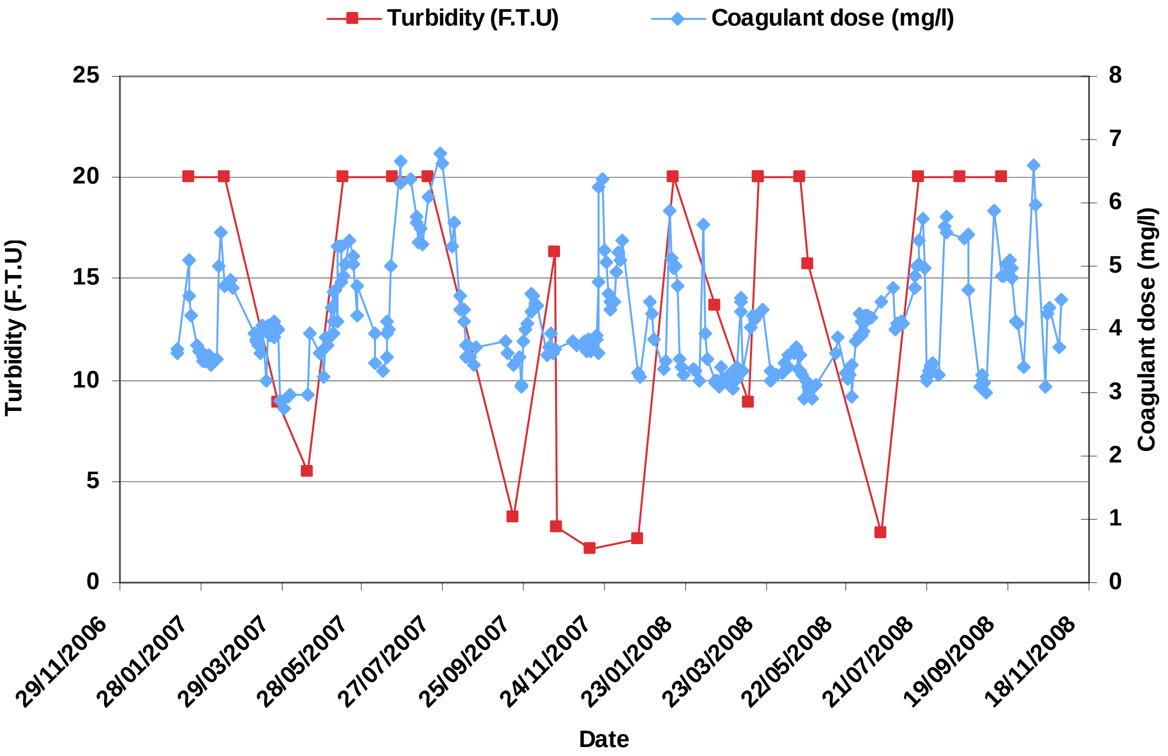


Figure 4.21; Raw water turbidity concentration (F.T.U) and coagulant dose at the pre-clarifier stage (mg/l Fe) between 2007 and 2008.

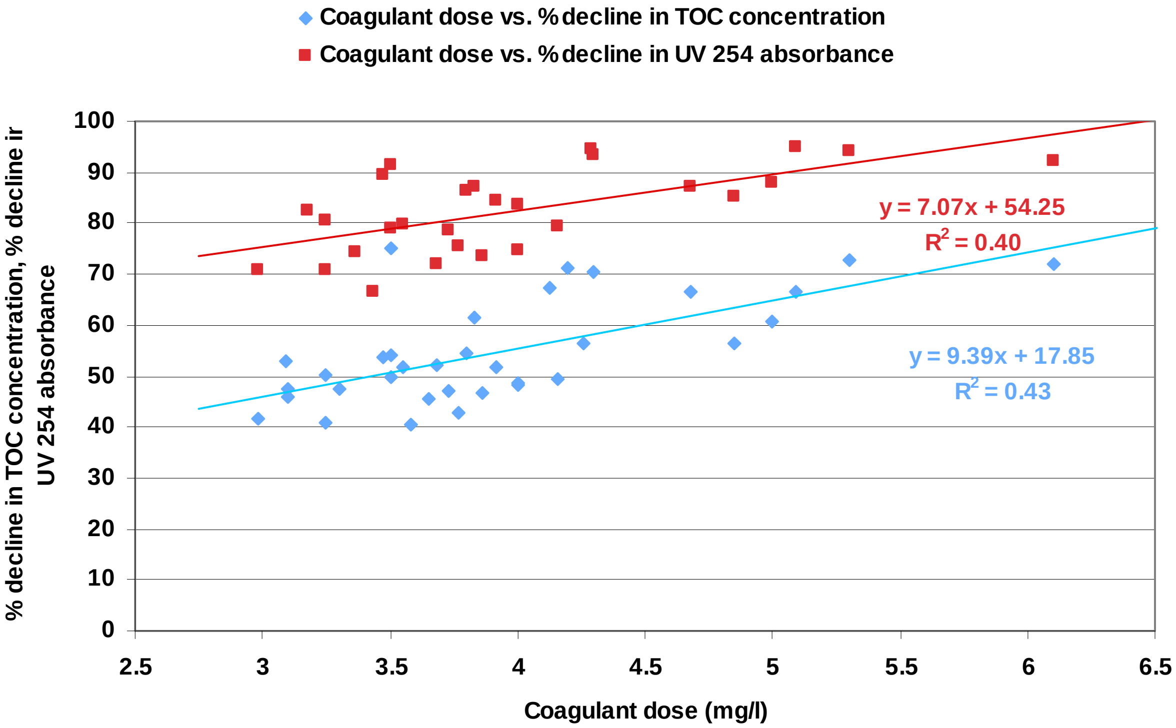


Figure 4.22; Percentage decline in UV_{254} absorbance and TOC concentration vs. coagulant dose at pre-clarifier (X-Y scatter plot with linear trend lines). Limited to when data was available for both raw / final water TOC concentrations and coagulant dosing data.

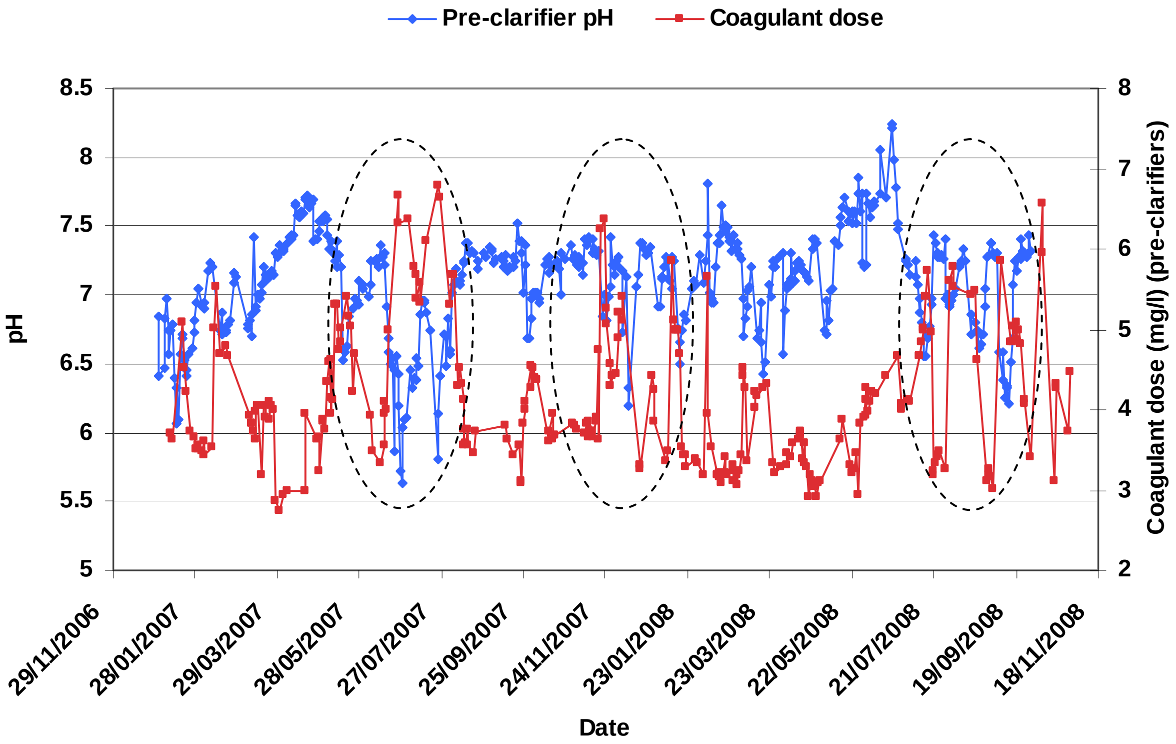


Figure 4.23; Coagulant dose and pre-clarifier pH between 2007 and 2008. Areas circled in dotted line highlight the co-ordination in high coagulant doses with lower coagulation pH.

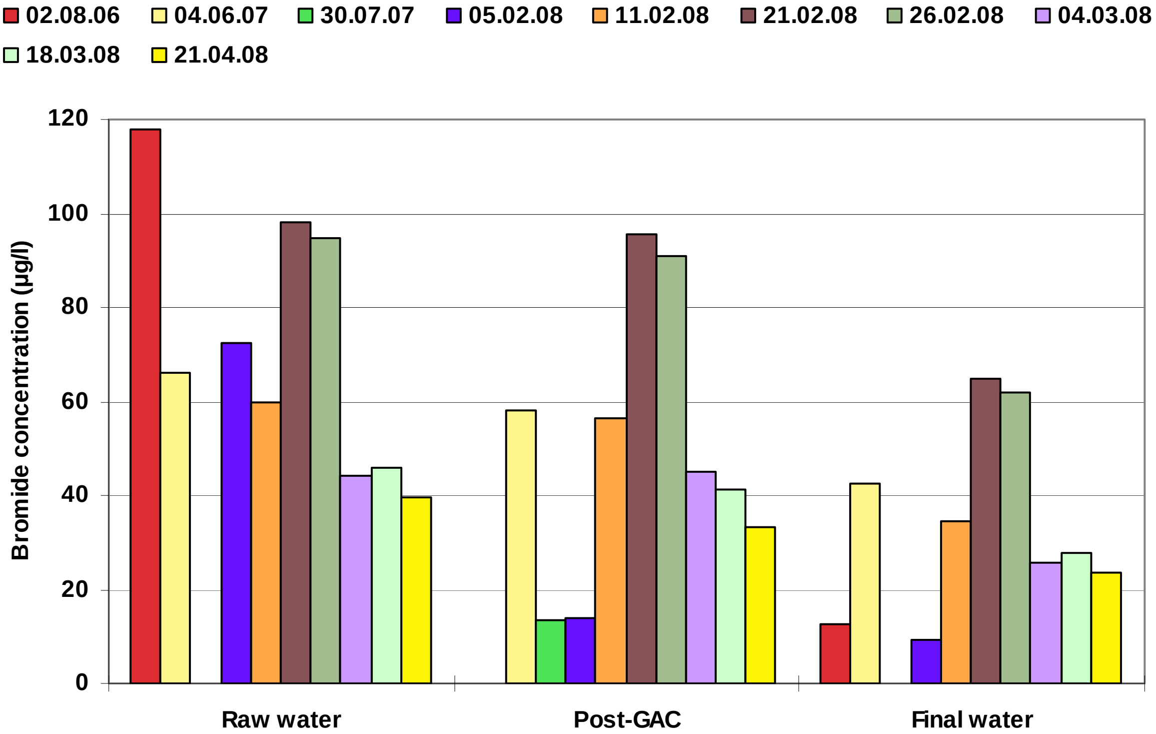


Figure 4.24; Bromide concentrations at the raw, post-GAC and final water sampling point on the days of sampling.

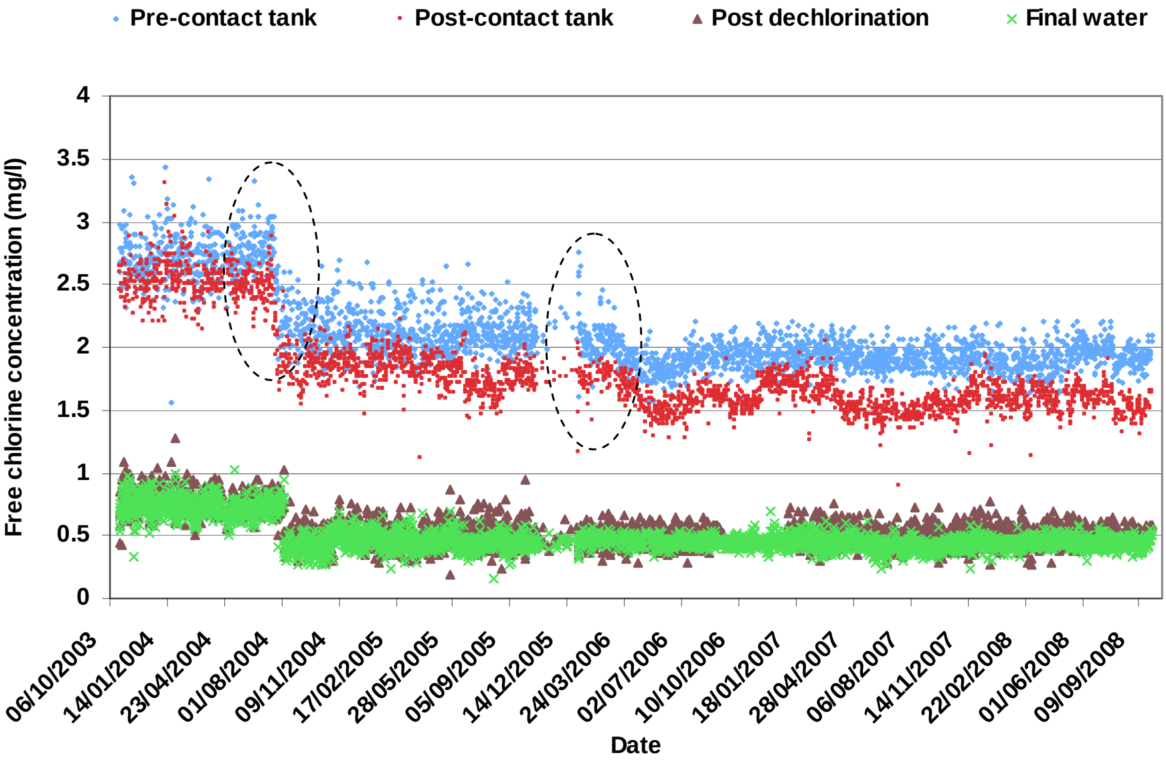


Figure 4.25; Free chlorine concentrations at sampling points through Strensham WTW between October 2003 and September 2008, with noted interventions circled.

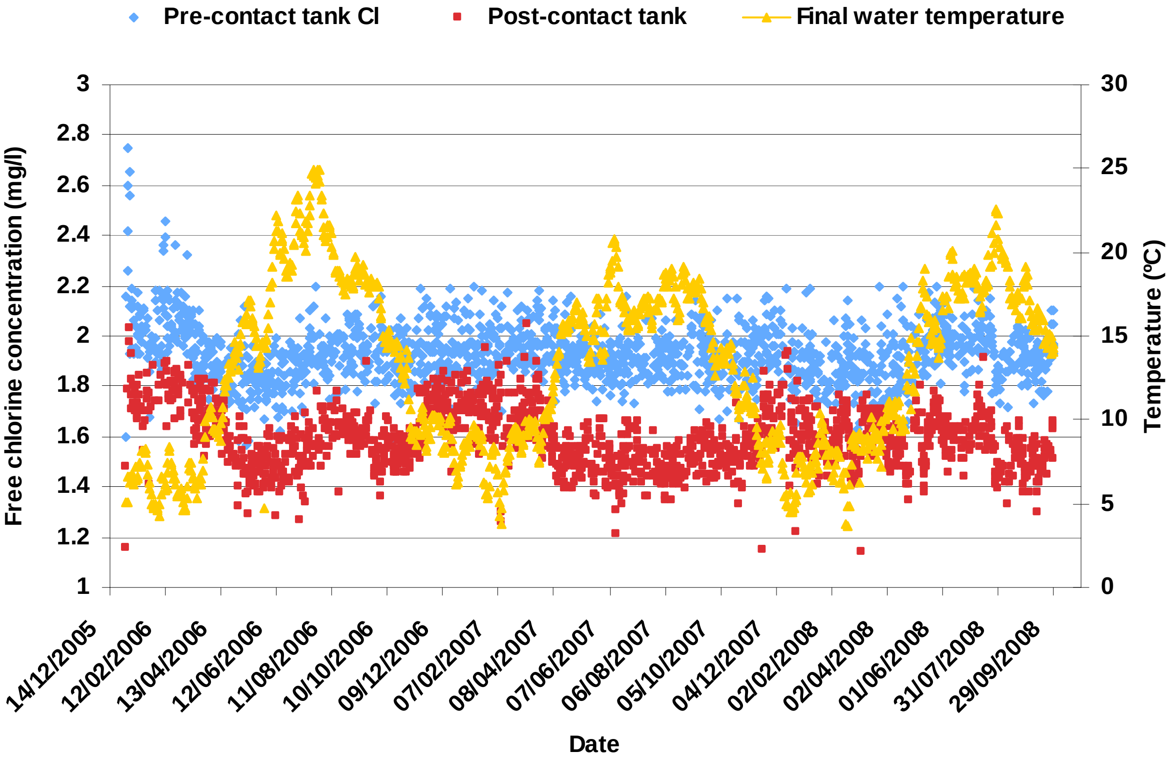


Figure 4.26; Pre-contact tank and post-contact tank free chlorine concentrations and final water temperature between 2006 and 2008.

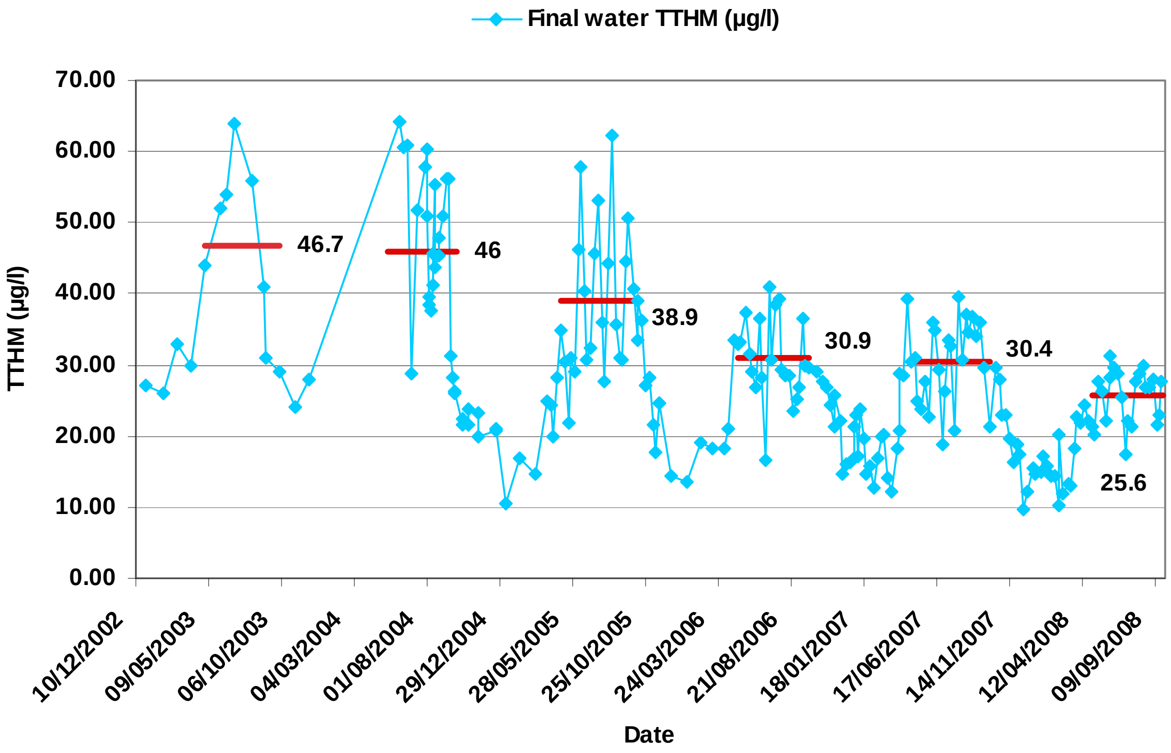


Figure 4.27; Final water TTHM concentrations between 2003 and 2008 at Strensham WTW, with summer averages (between start May and end September).

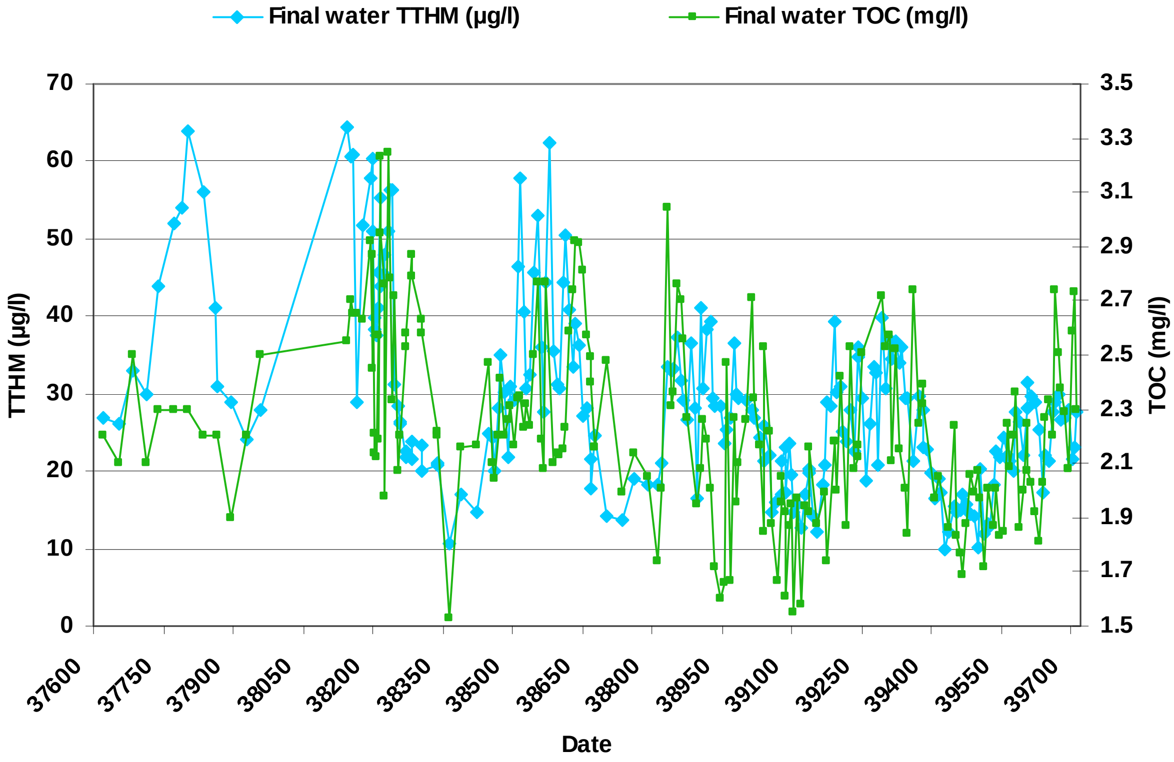


Figure 4.28; Final water TTHM concentrations (L.H.S. axis) and TOC concentrations (R.H.S. axis) between 2003 and 2008.

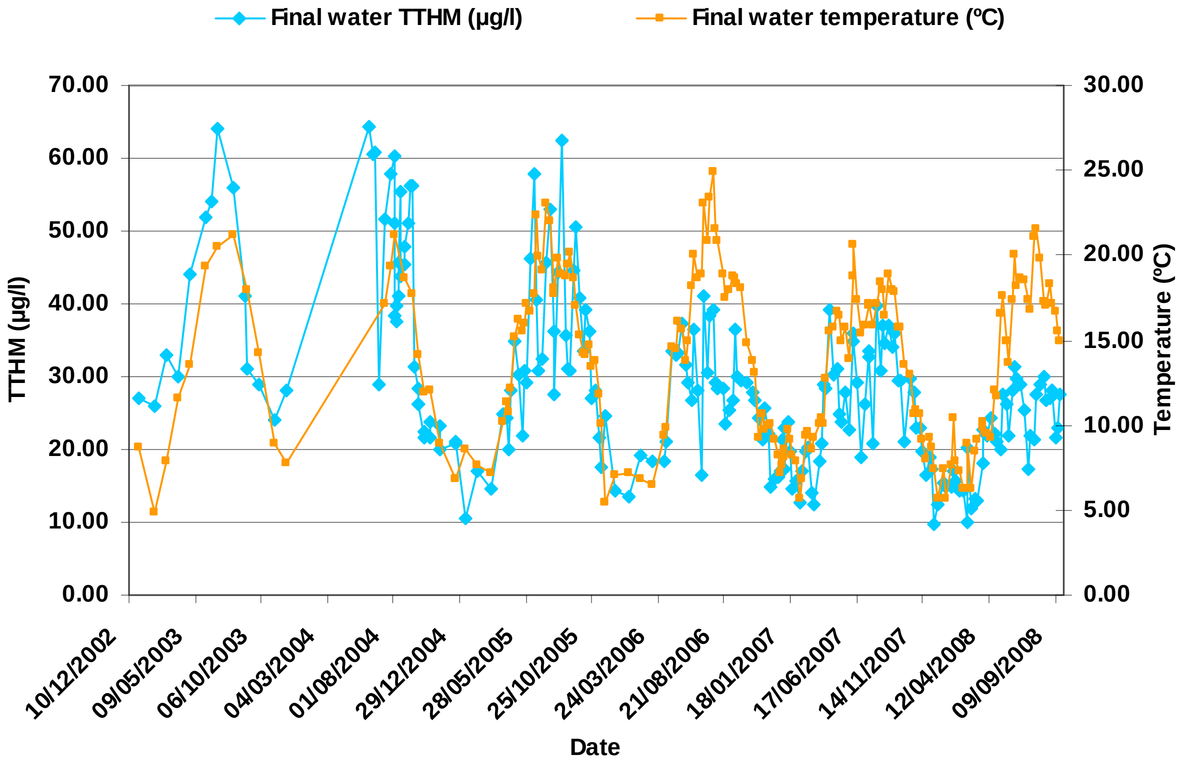


Figure 4.29; Final water TTHM concentrations (L.H.S. axis) and temperature (R.H.S. axis) between 2003 and 2008.

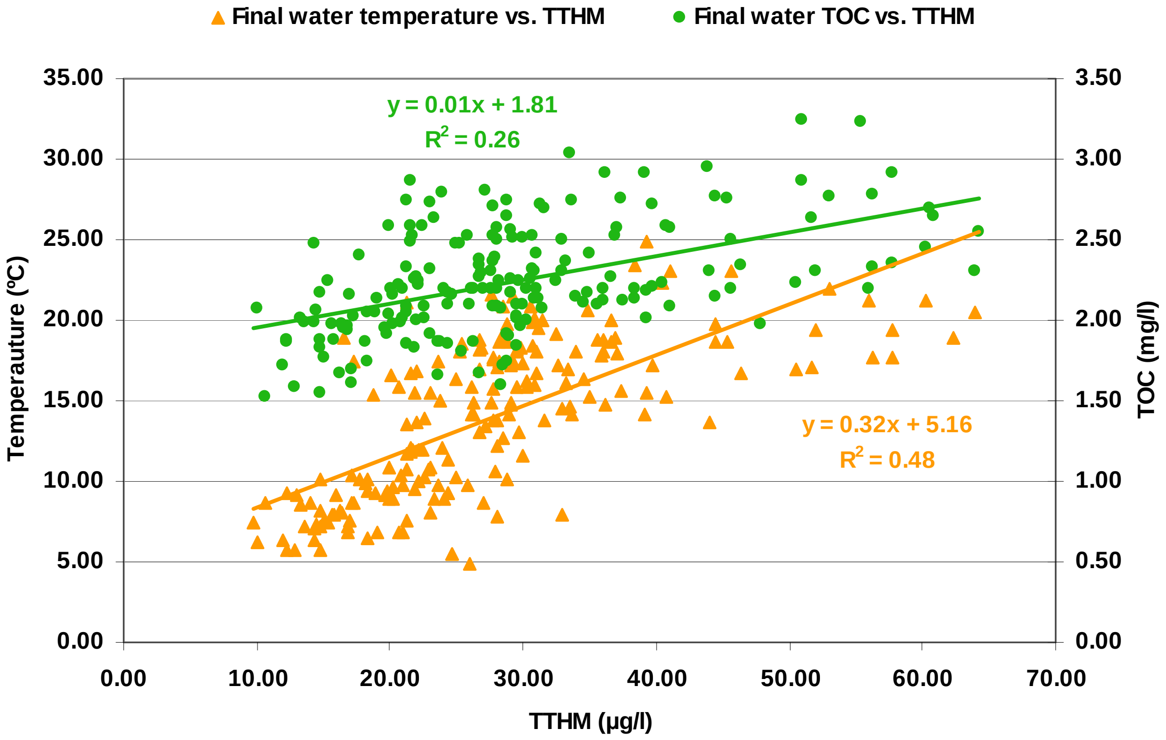


Figure 4.30; Final water TTHM concentrations vs. final water TOC concentrations + Final water TTHM concentrations vs. final water temperature (both X-Y scatter plots with linear trend lines) (on different y-axis).

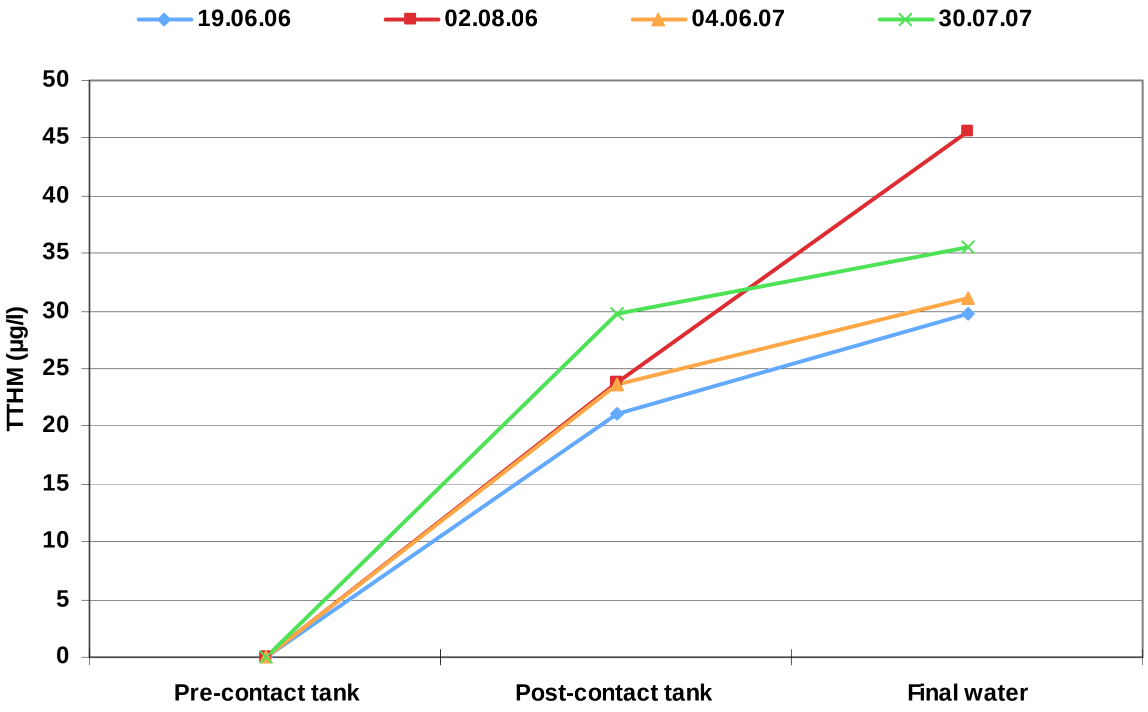


Figure 4.31; TTHM concentrations through Strensham WTW from summer sampling days.

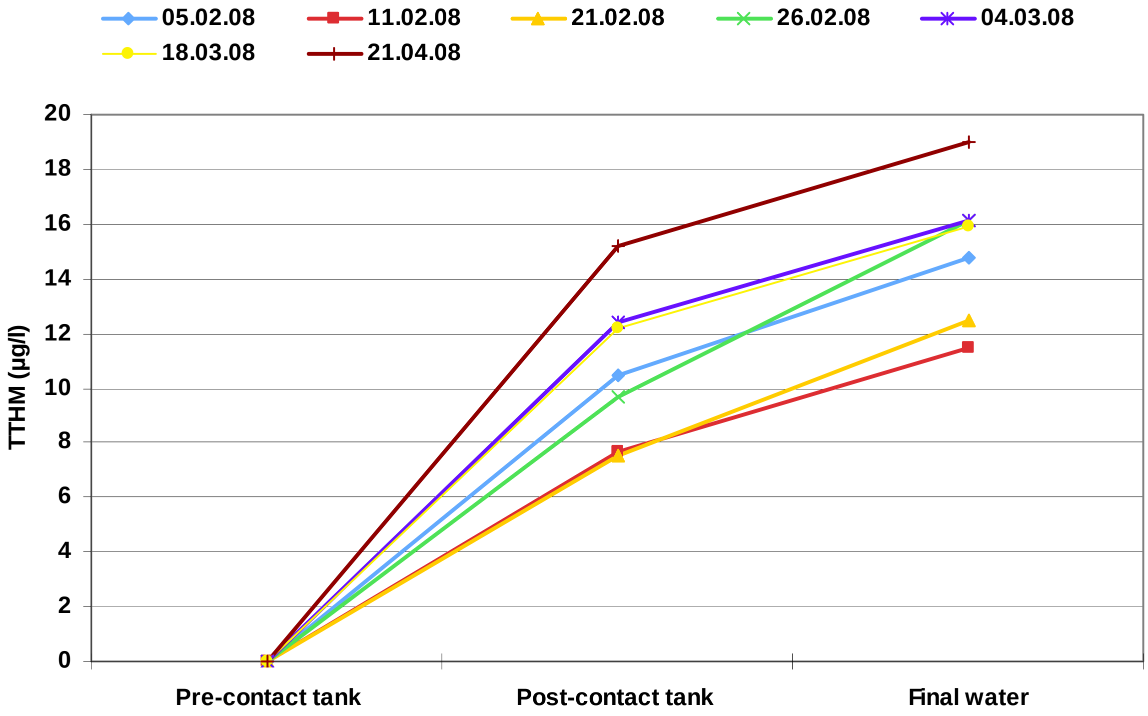


Figure 4.32; TTHM concentrations through Strensham WTW from Spring sampling days.

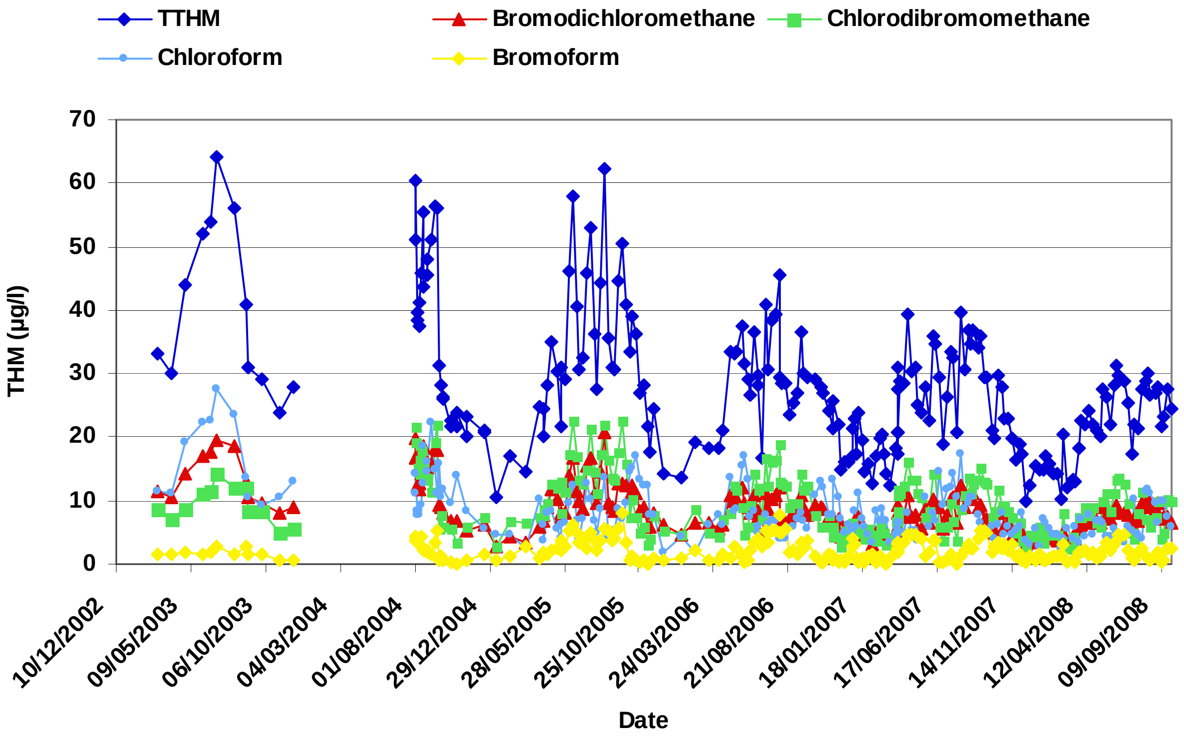


Figure 4.33; TTHM (and four main THM species) at final water sampling point at Strensham WTW, between 2003 – 2008.

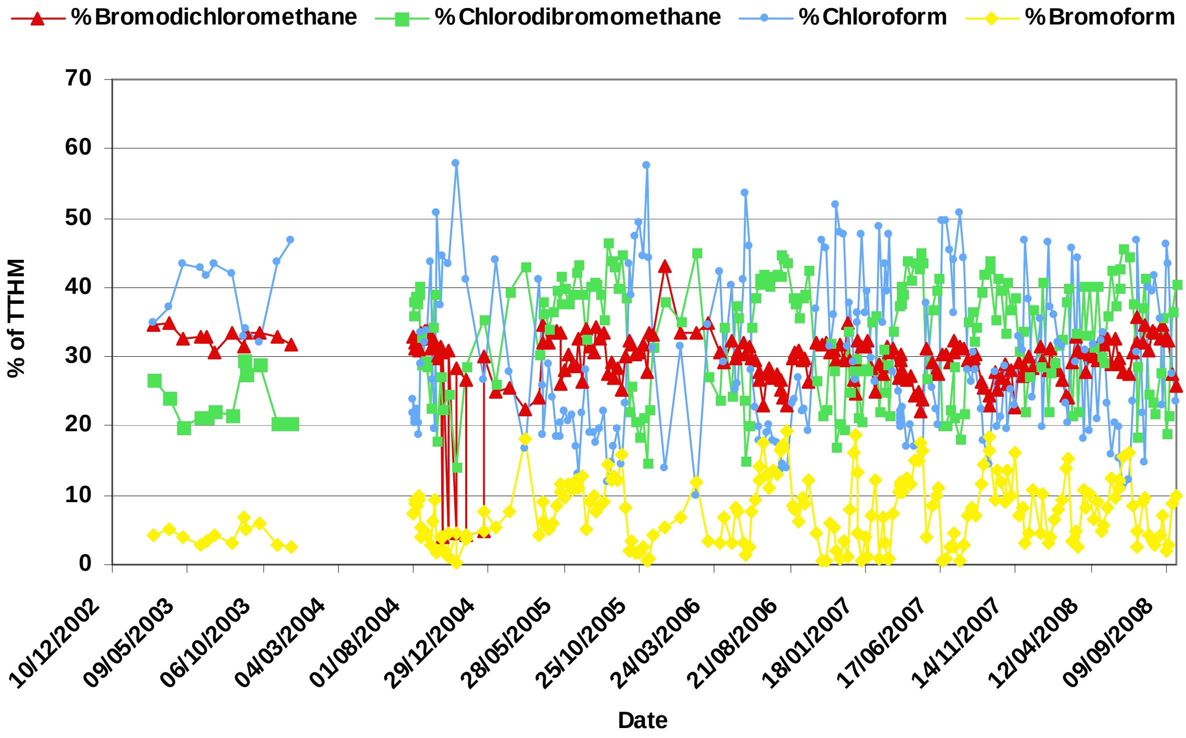


Figure 4.34; Individual THM species as a percentage of TTHM at Strensham WTW final water between start of 2003 and end September 2008.

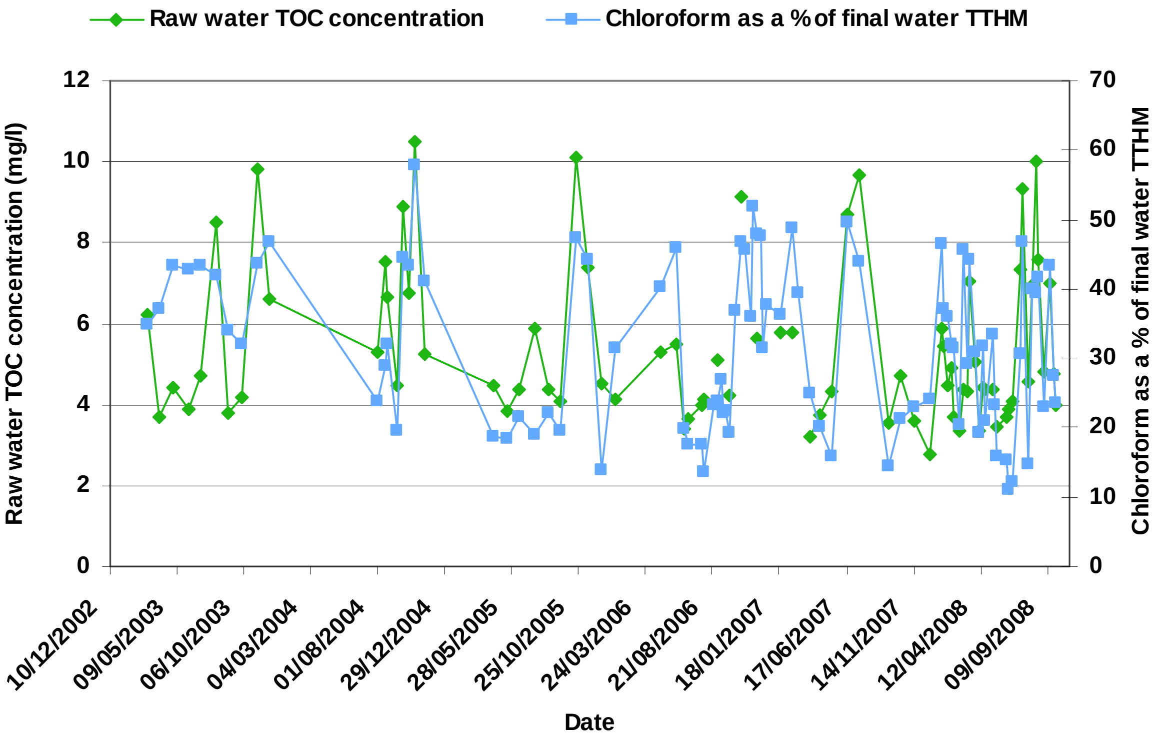


Figure 4.35; Raw water TOC concentrations and the percentage of TTHM which is chloroform at final water sampling point at Strensham WTW, between 2003 – 2008.

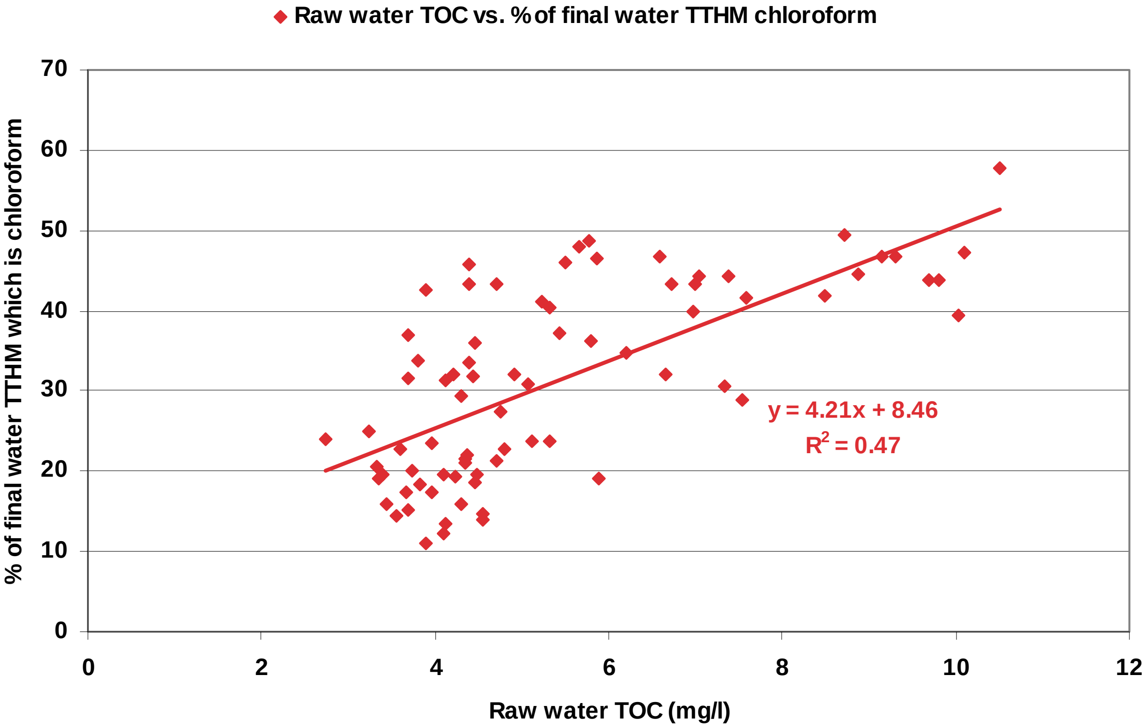


Figure 4.36; Chloroform as a % of TTHM at Strensham final water vs. raw water TOC concentrations (X-Y scatter plot) – based solely on samples where THM and TOC concentrations taken on same days.

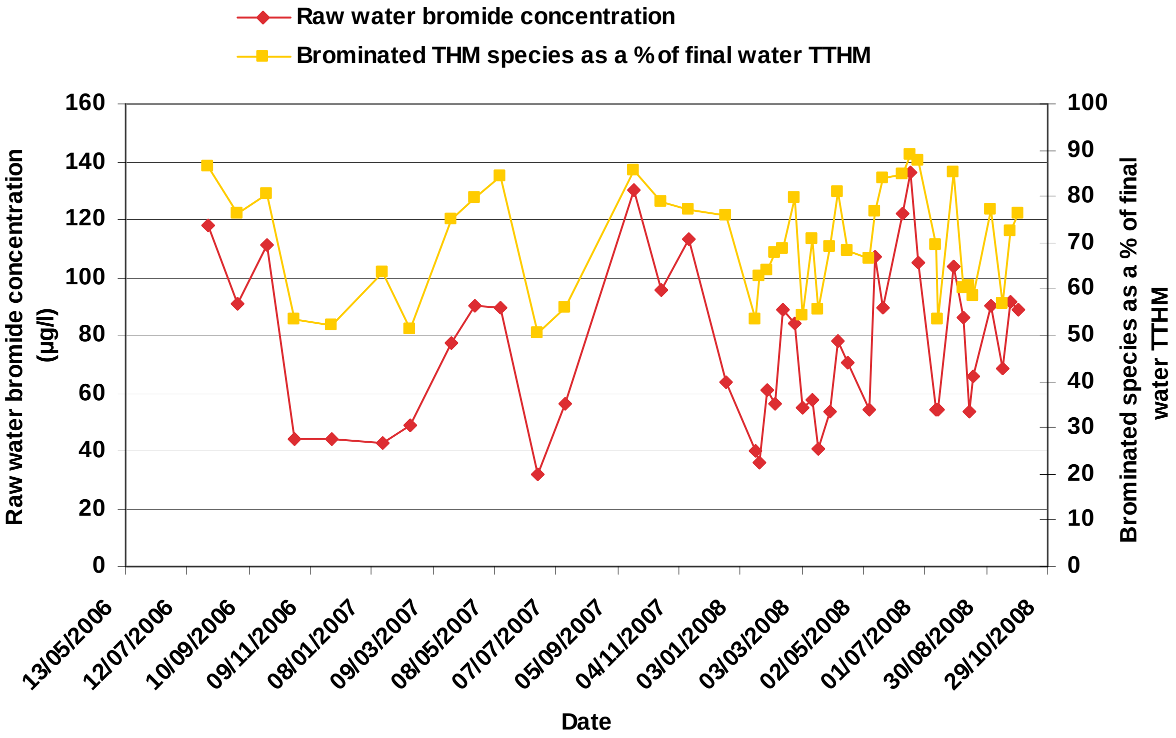


Figure 4.37; Raw water bromide concentrations and percentage of TTHM which are brominated species ($CHBr_2Cl$, $CHBrCl_2$ & $CHBr_3$) at Strensham Final water.

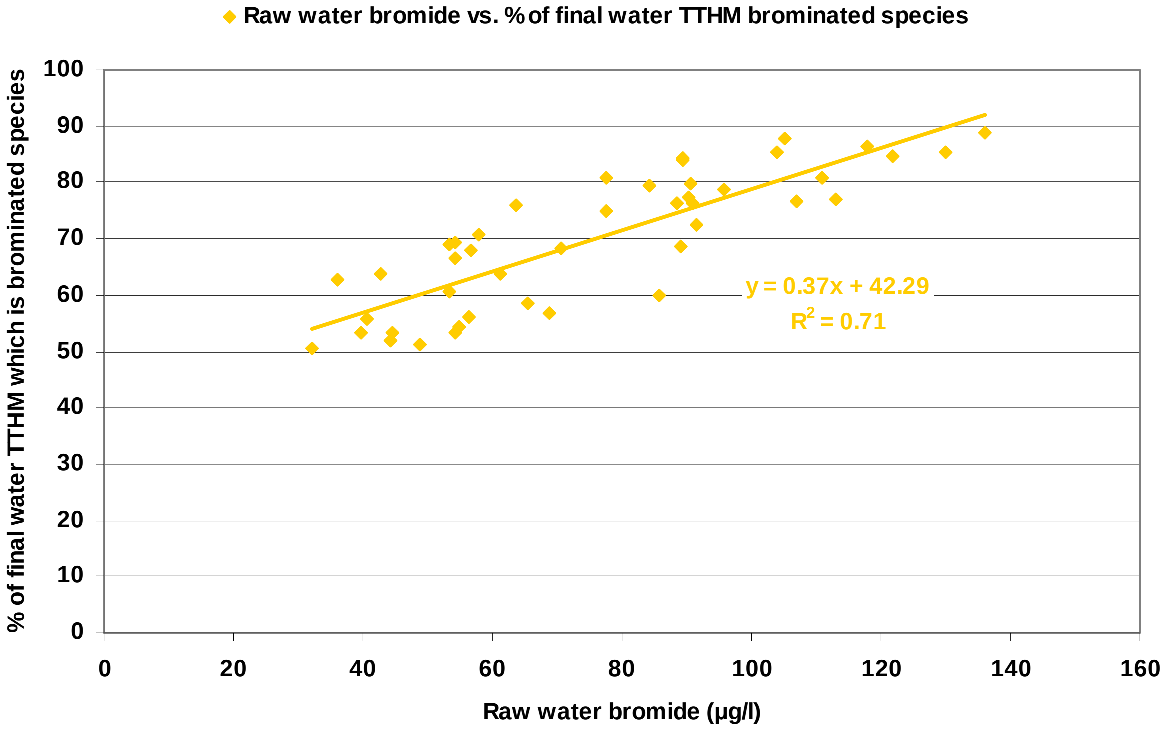


Figure 4.38; Brominated ($CHBr_2Cl$, $CHBrCl_2$ & $CHBr_3$) species as a % of TTHM at Strensham final water vs. raw water bromide concentrations (X-Y scatter plot) – based solely on samples where THM and bromide concentrations sampled on same days.

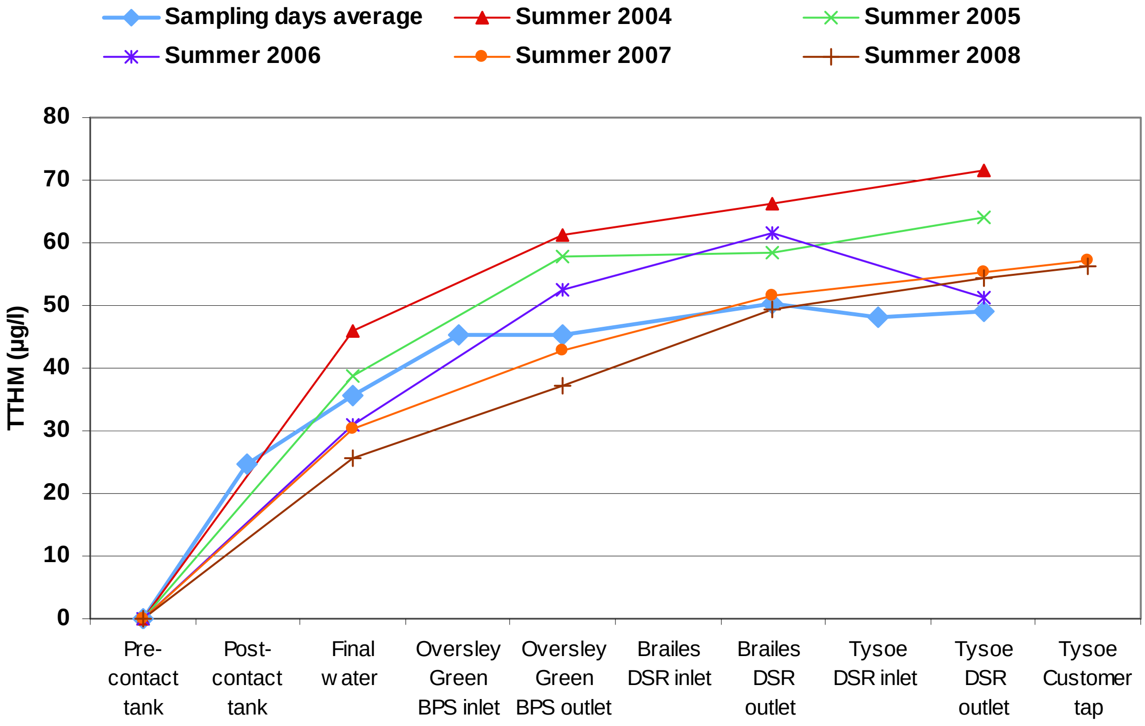


Figure 4.39; THM concentrations through Strensham WTW and Shipston distribution based on sampling day averages from summer 2006 / 2007, and annual summer averages.

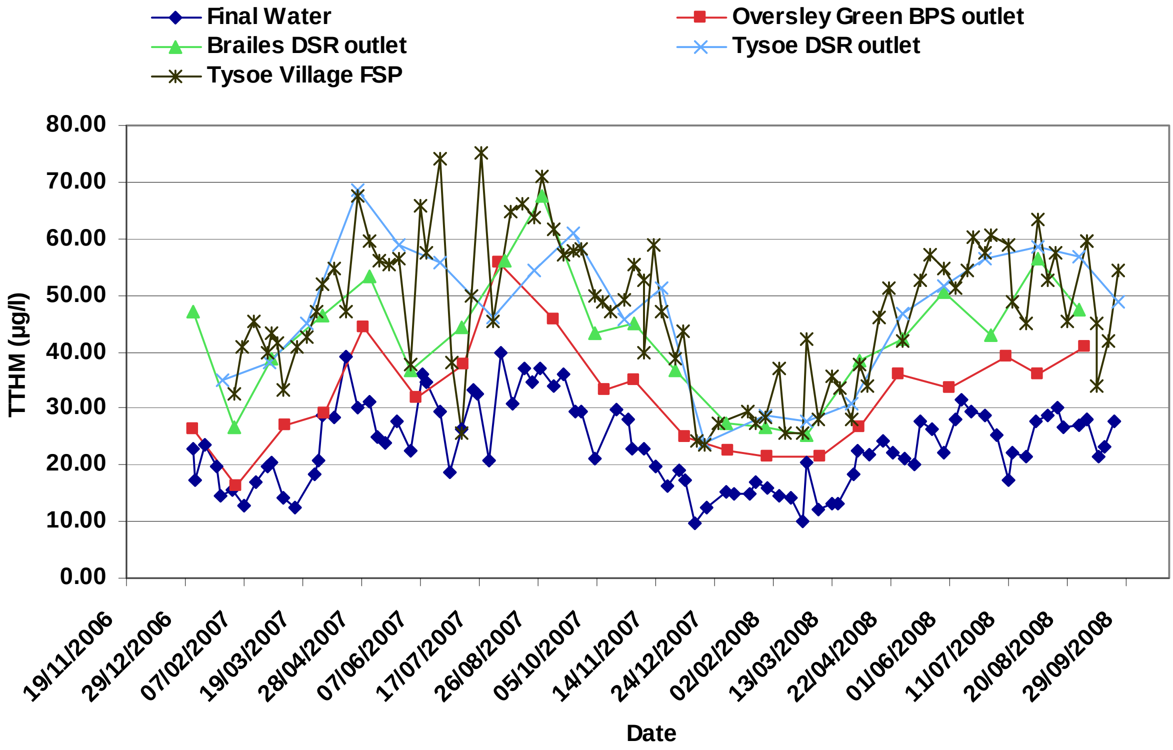


Figure 4.40; TTHM concentrations at Strensham final water and service reservoirs in Shipston distribution (Tysoe leg).

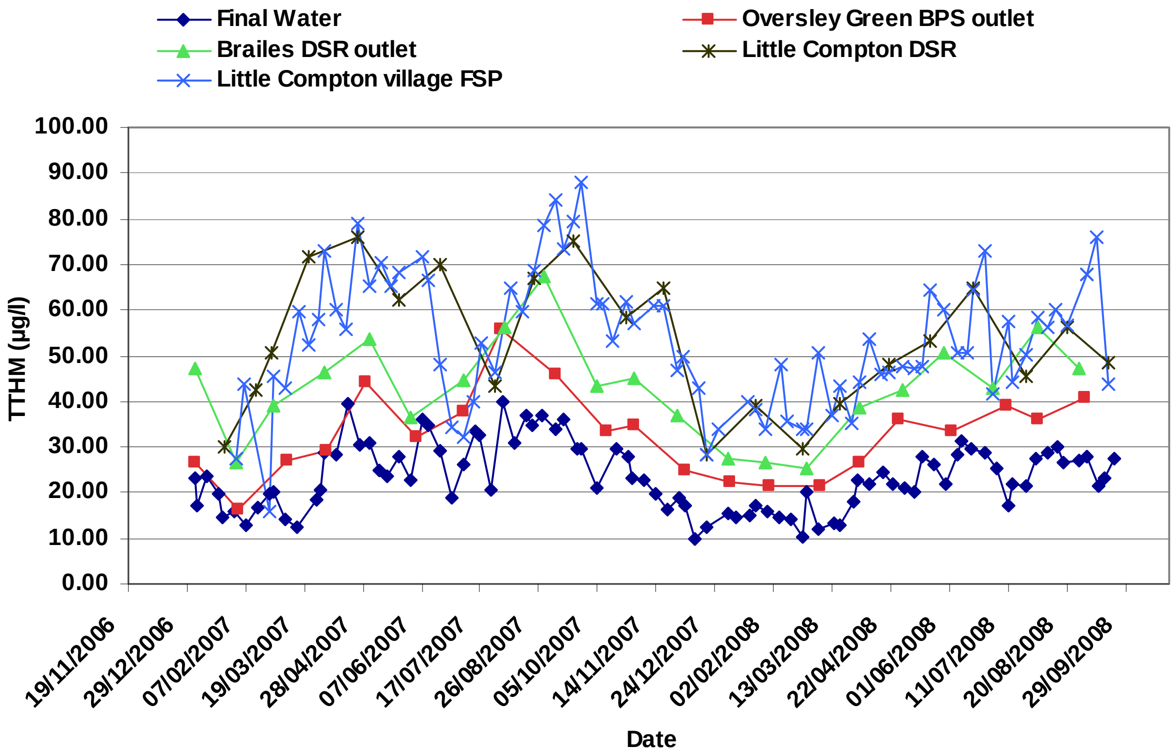


Figure 4.41; TTHM concentrations at Strensham final water and service reservoirs in Shipston distribution (Little Compton leg).

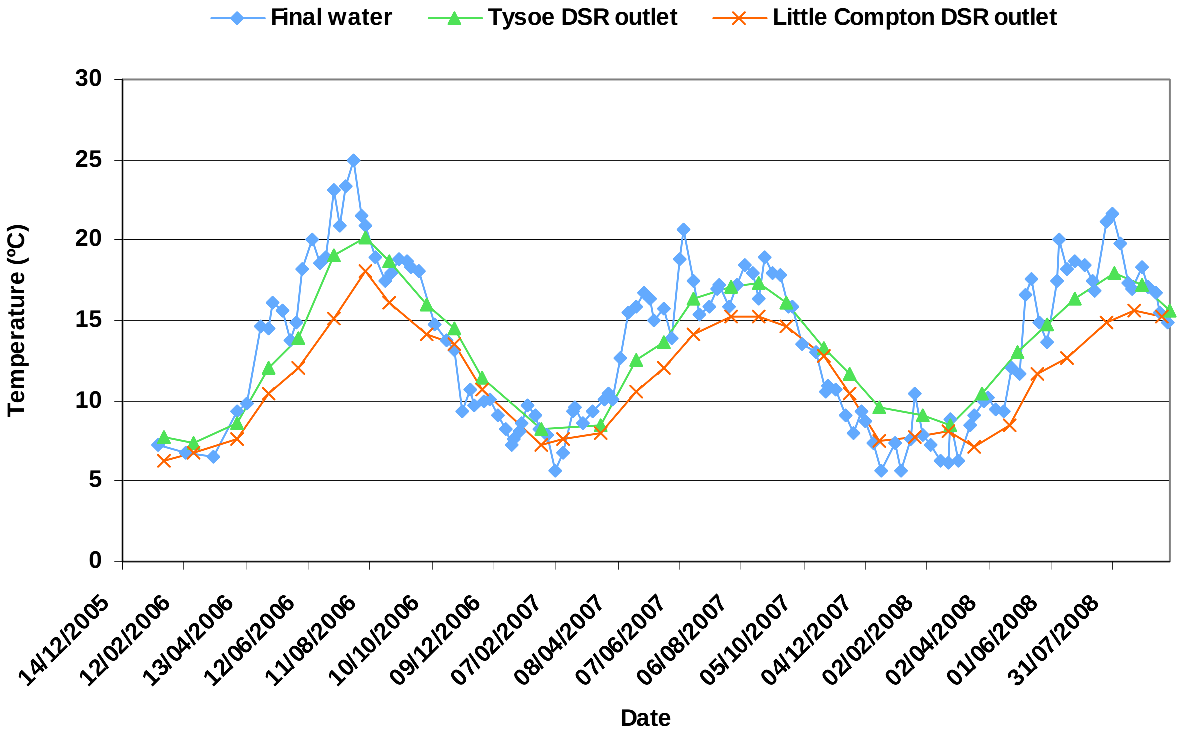


Figure 4.42; Temperature at Strensham WTW final water and Tysoe and Little Compton DSR outlets, between 2006 – 2008.

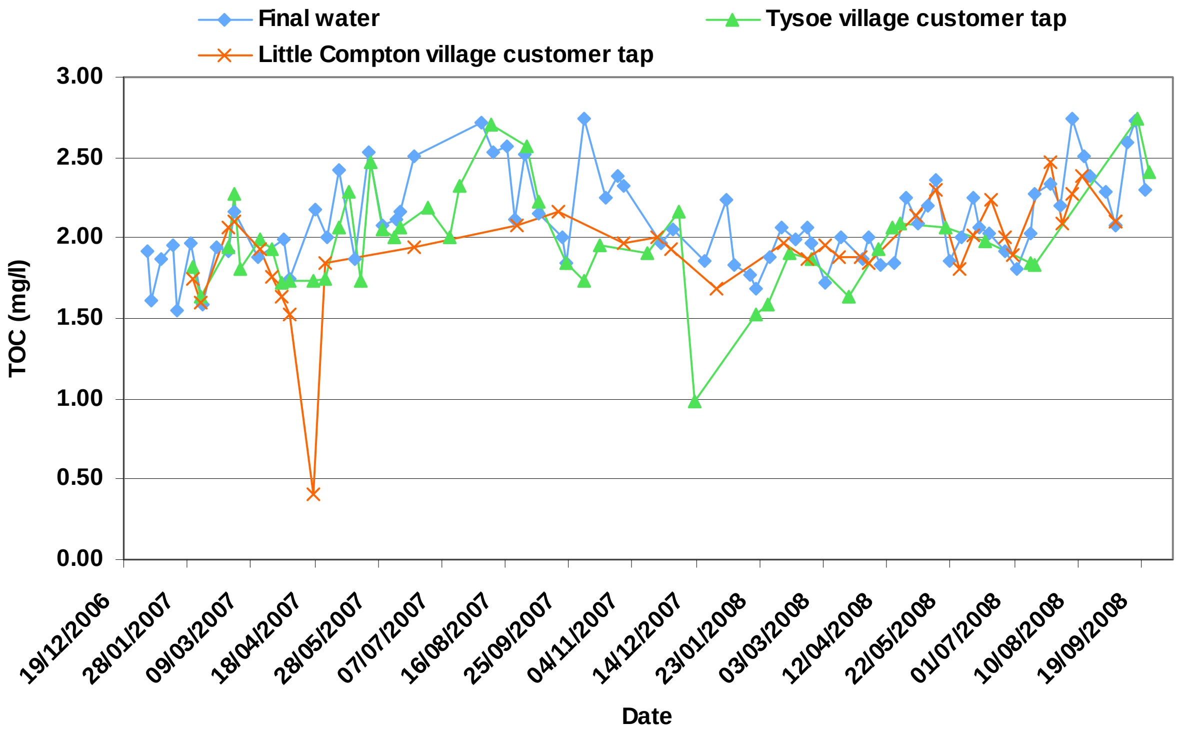


Figure 4.43; TOC concentrations at Strensham WTW and Tysoe / Little Compton village customer taps, between 2006 – 2008.

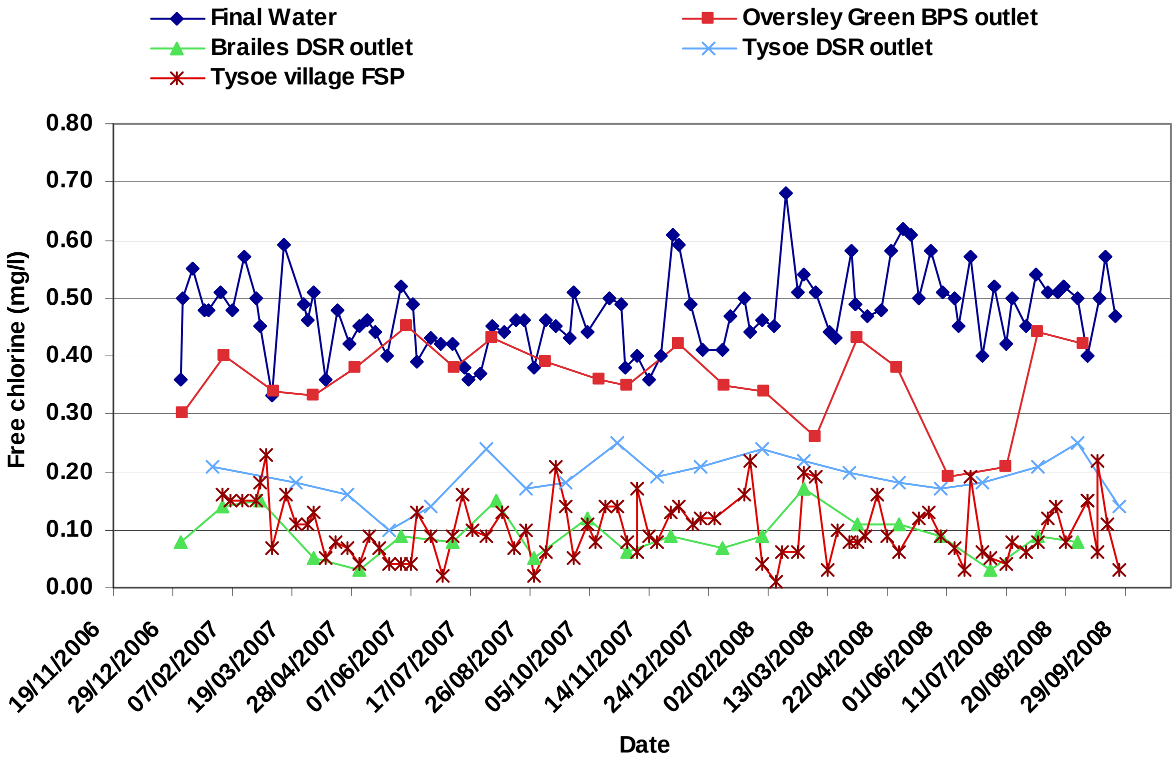


Figure 4.44; Free chlorine concentrations at Strensham final water and service reservoirs in Shipston distribution (Tysoe leg), between 2006 and 2008.

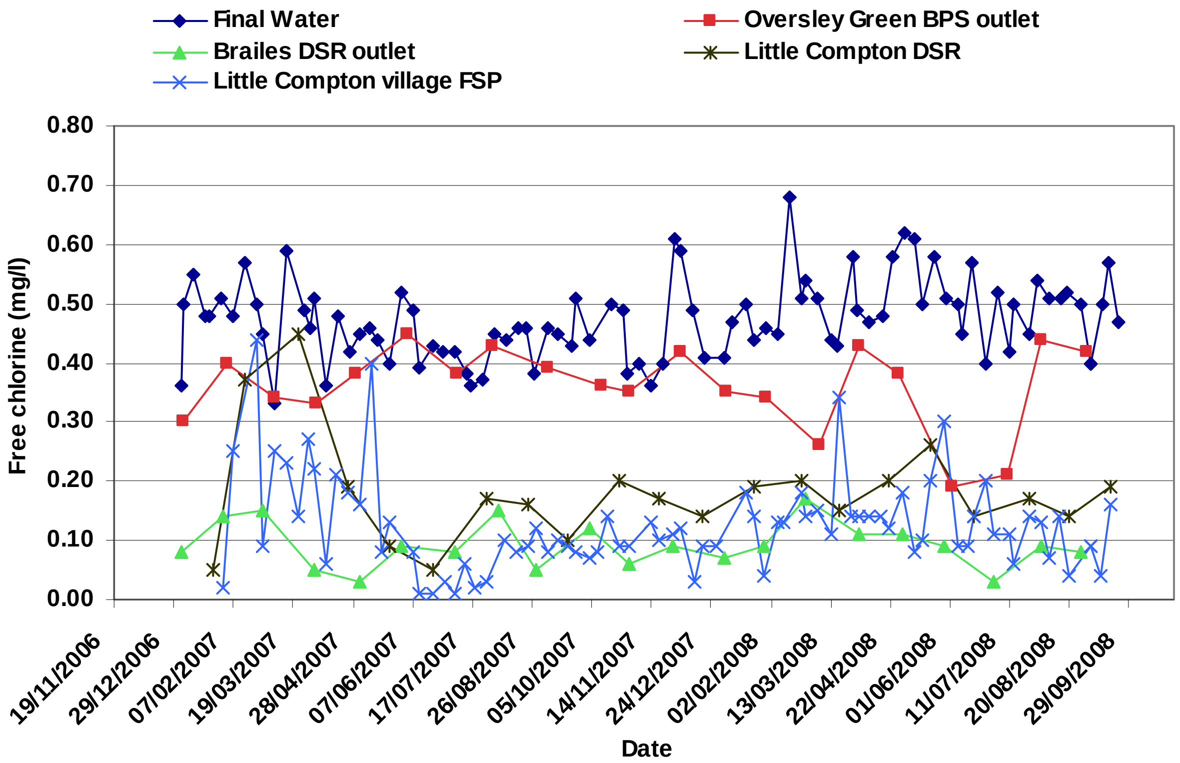


Figure 4.45; Free chlorine concentrations at Strensham final water and service reservoirs in Shipston distribution (Little Compton leg), between 2006 and 2008.

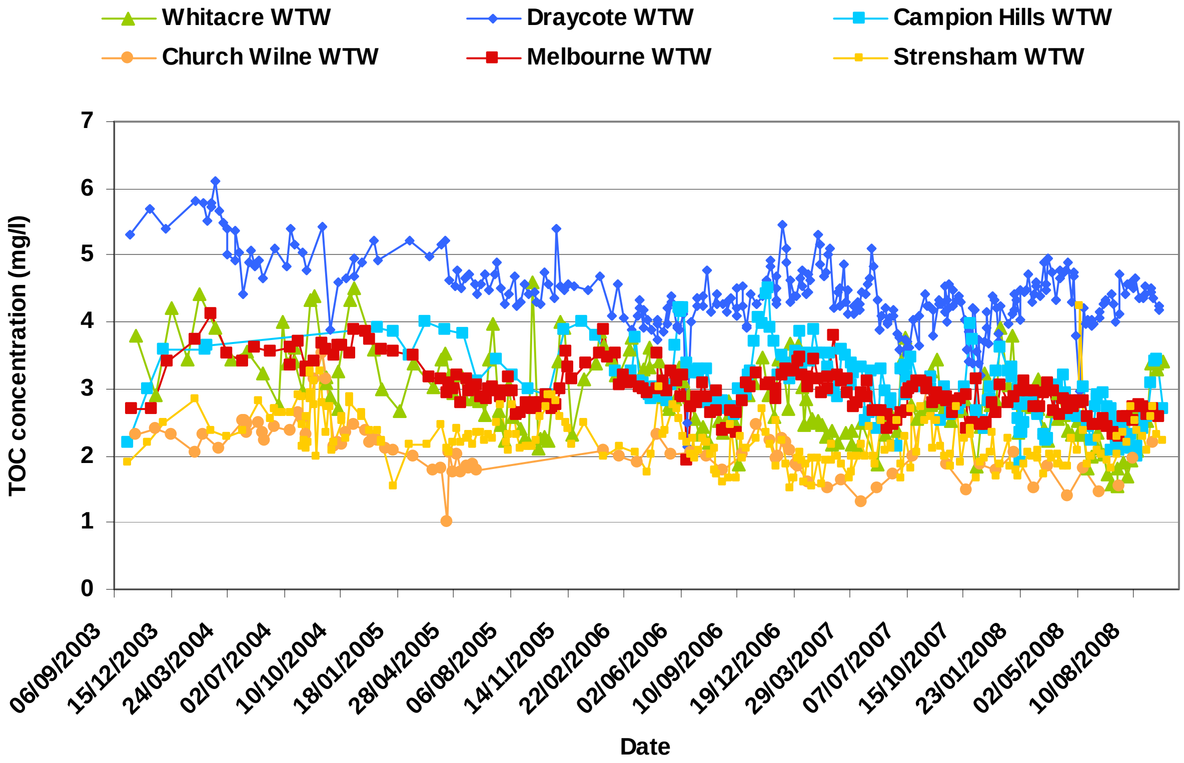


Figure 4.46; Raw water TOC concentrations entering six WTWs between October 2003 and September 2008.

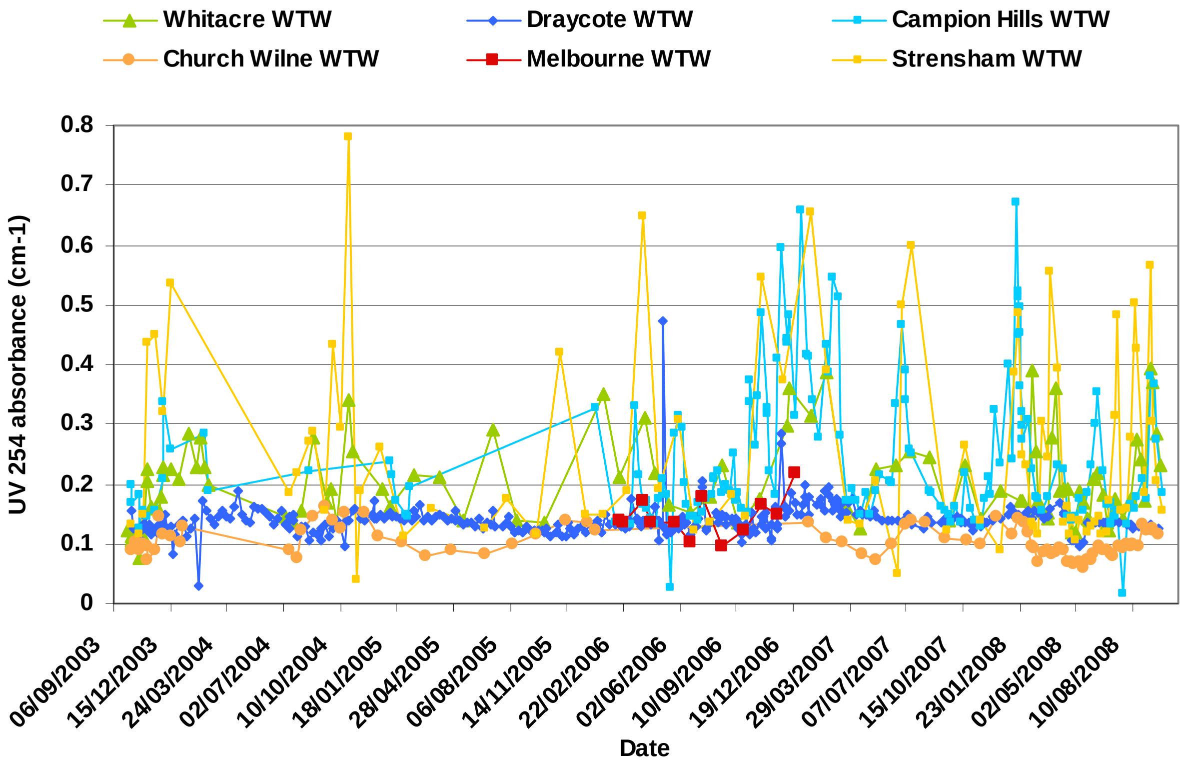


Figure 4.47; Raw water UV_{254} absorbance concentrations entering six WTWs between October 2003 and September 2008.

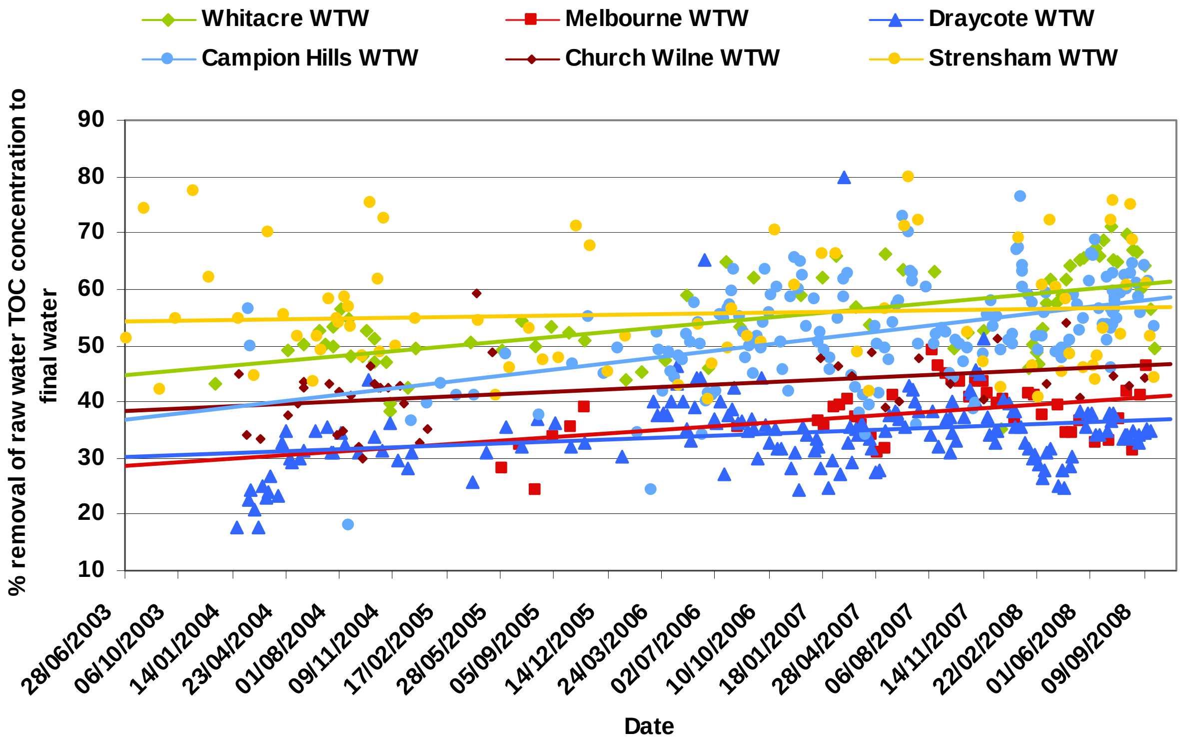


Figure 4.48; Percentage TOC removals across the WTW from raw water to final water TOC concentrations at six WTWs.

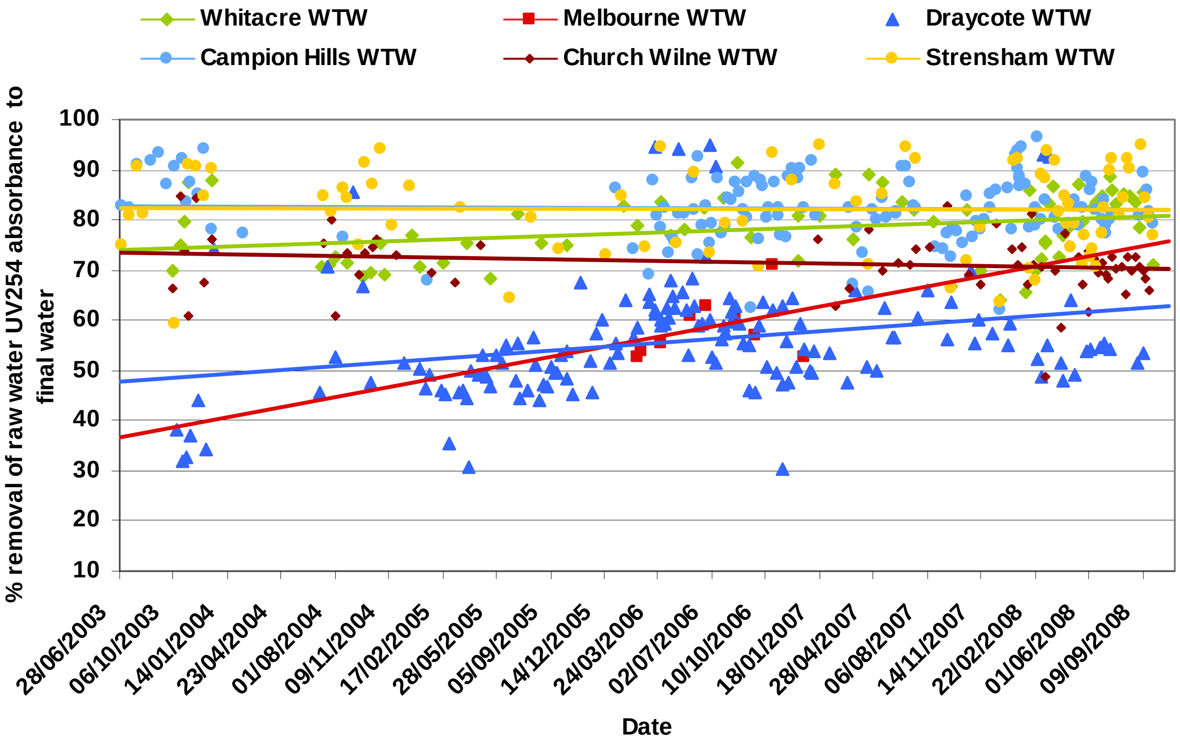


Figure 4.49; Percentage removals of UV_{254} absorbance levels across the WTW from raw water to final water TOC concentrations at six WTWs.

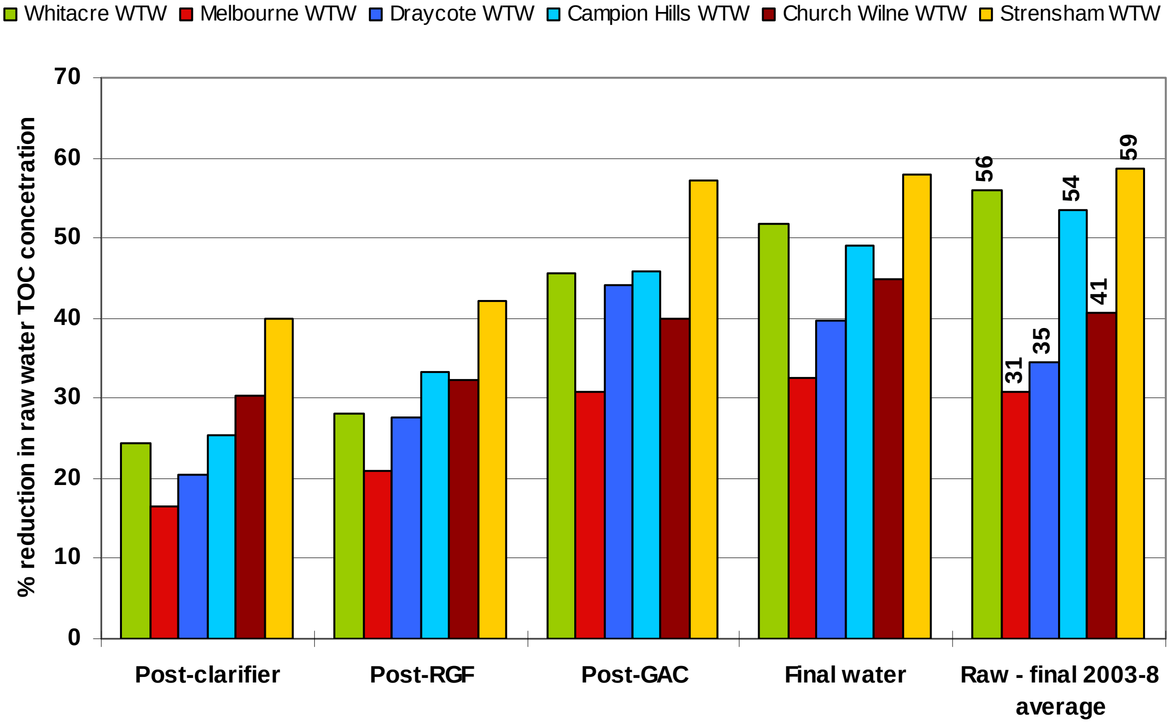


Figure 4.50; Percentage reduction in raw water TOC concentrations to selected points through 6 WTWs (x-axis) and average reduction from raw to final water between 2003 – 2008 (far right).

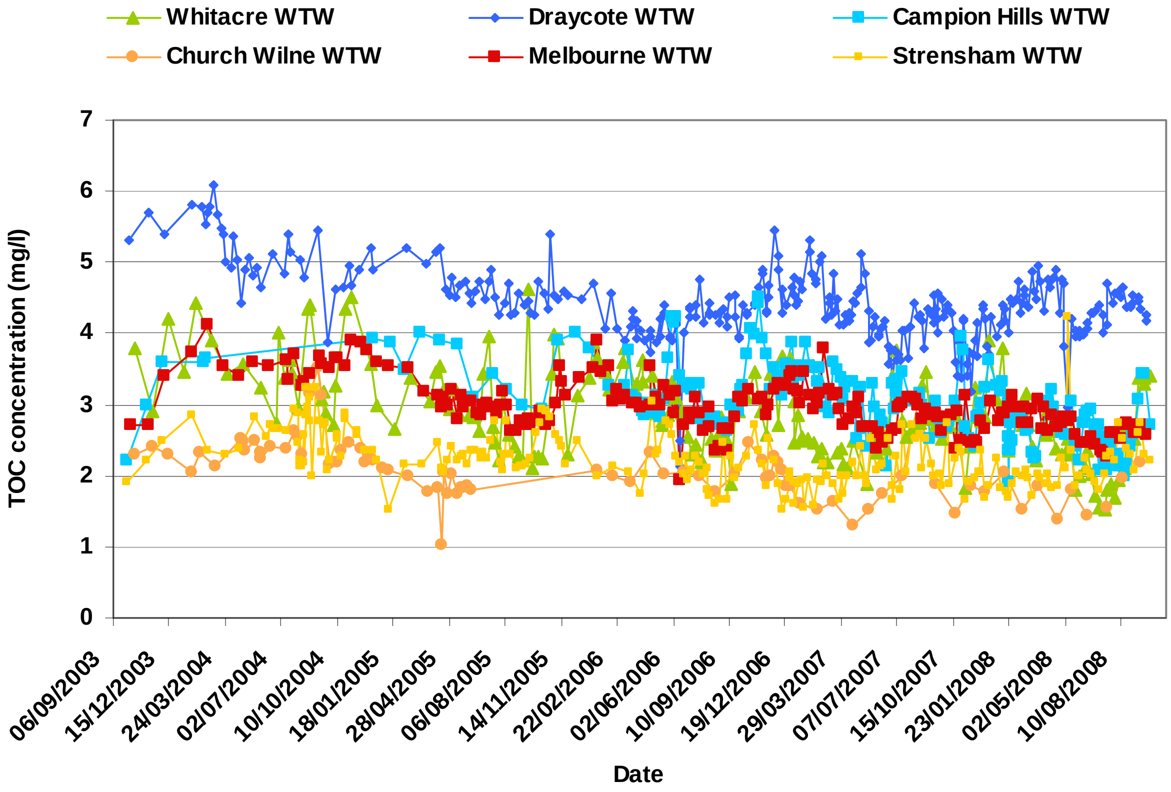


Figure 4.51; Final water TOC concentrations at six WTWs between October 2003 and September 2008.

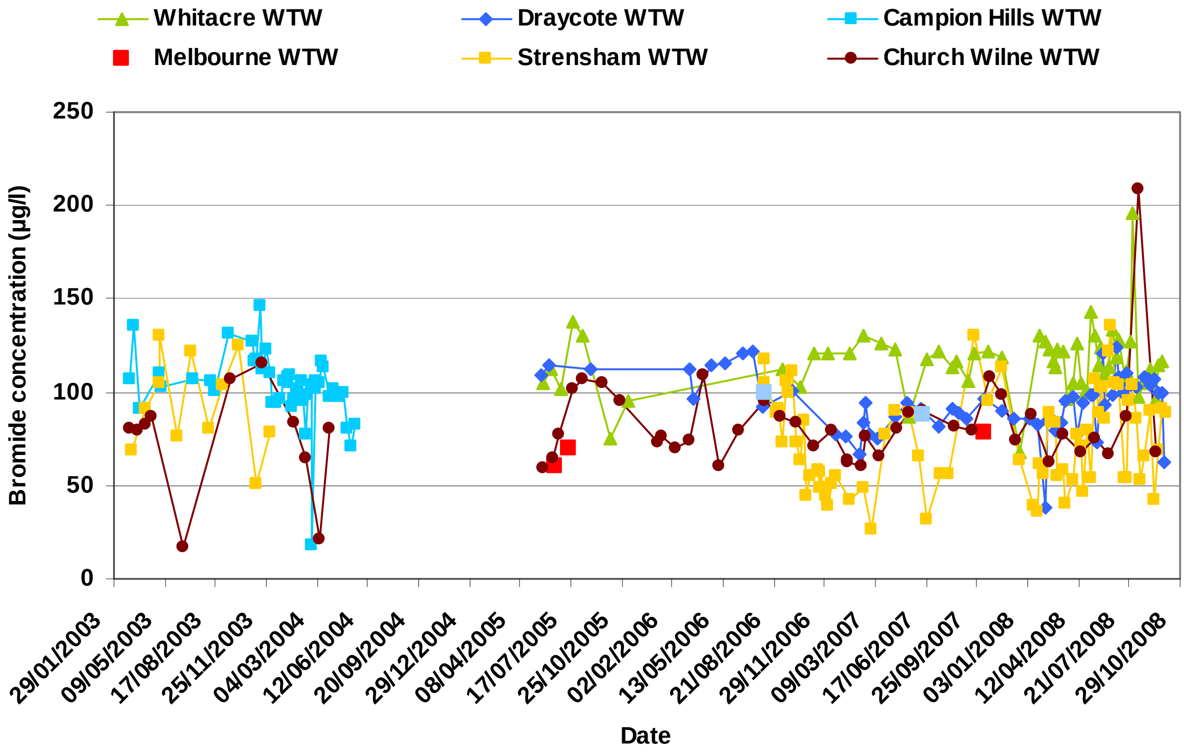


Figure 4.52; Raw water bromide concentrations entering 6 WTWs between January 2003 and September 2008.

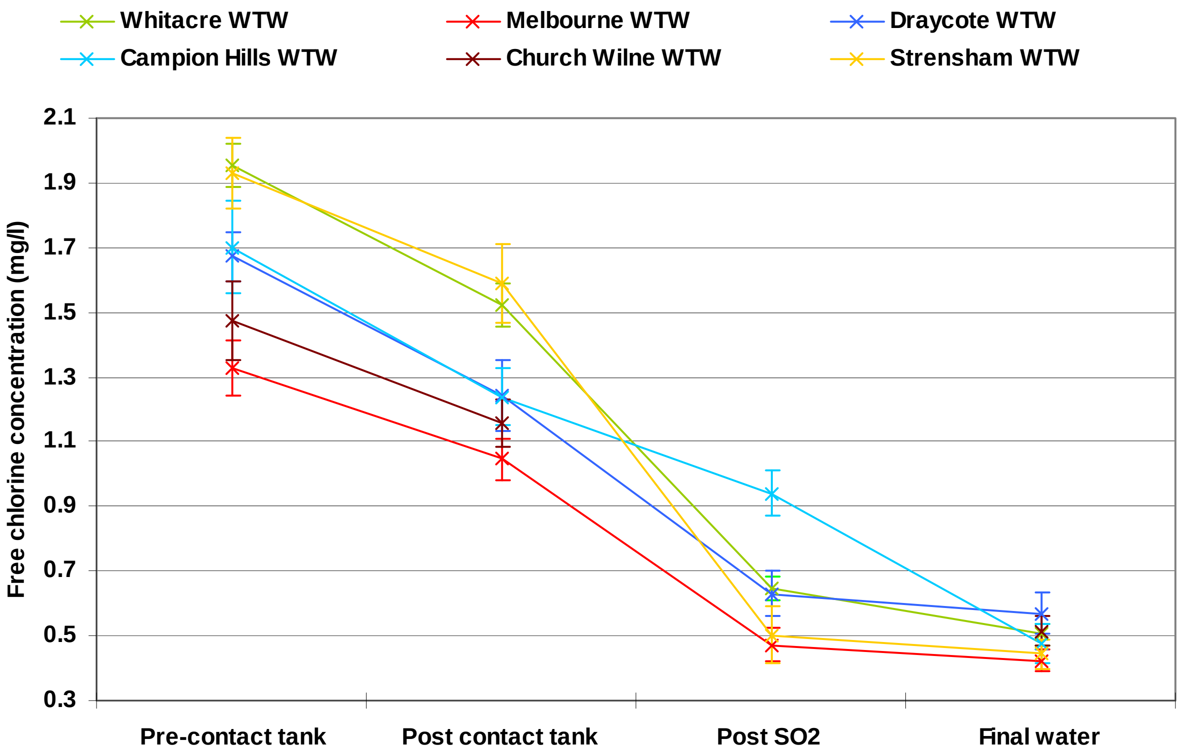


Figure 4.53; Average free chlorine concentrations (± 1 standard deviation) through six WTWs between start 2006 and end September 2008.

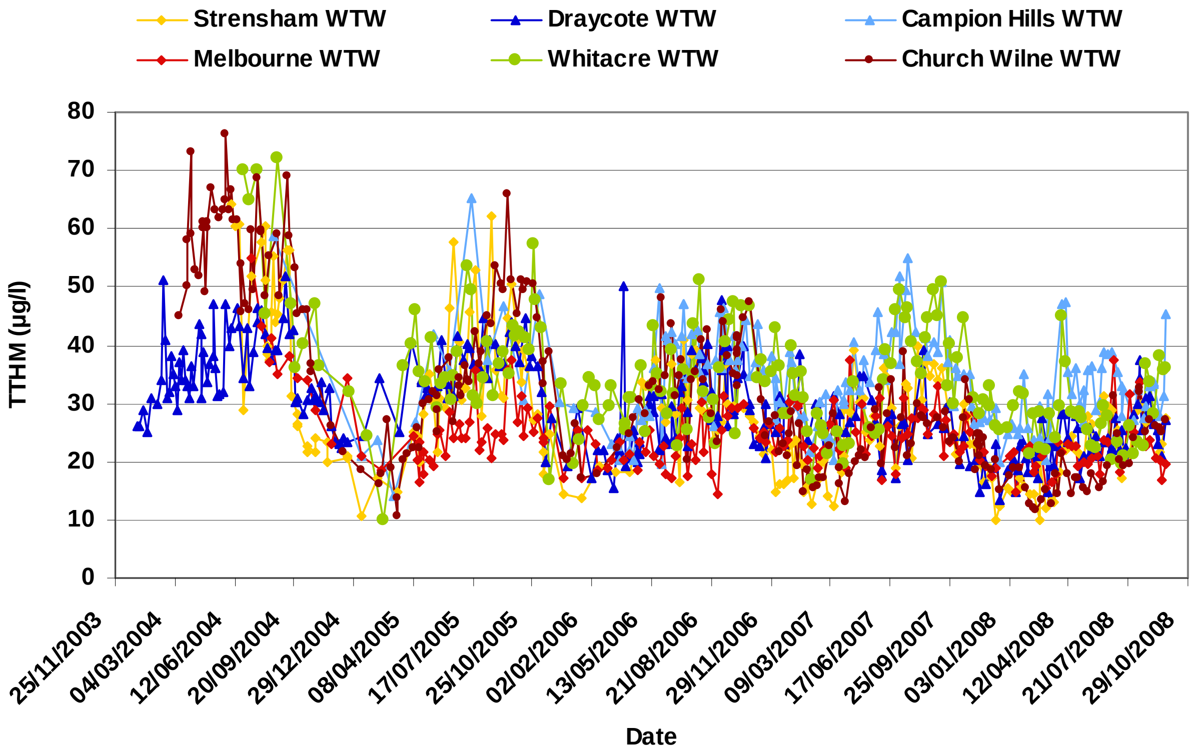


Figure 4.54; TTHM concentrations at the final water at each of the six WTWs between the start of 2004 and end of September 2008.

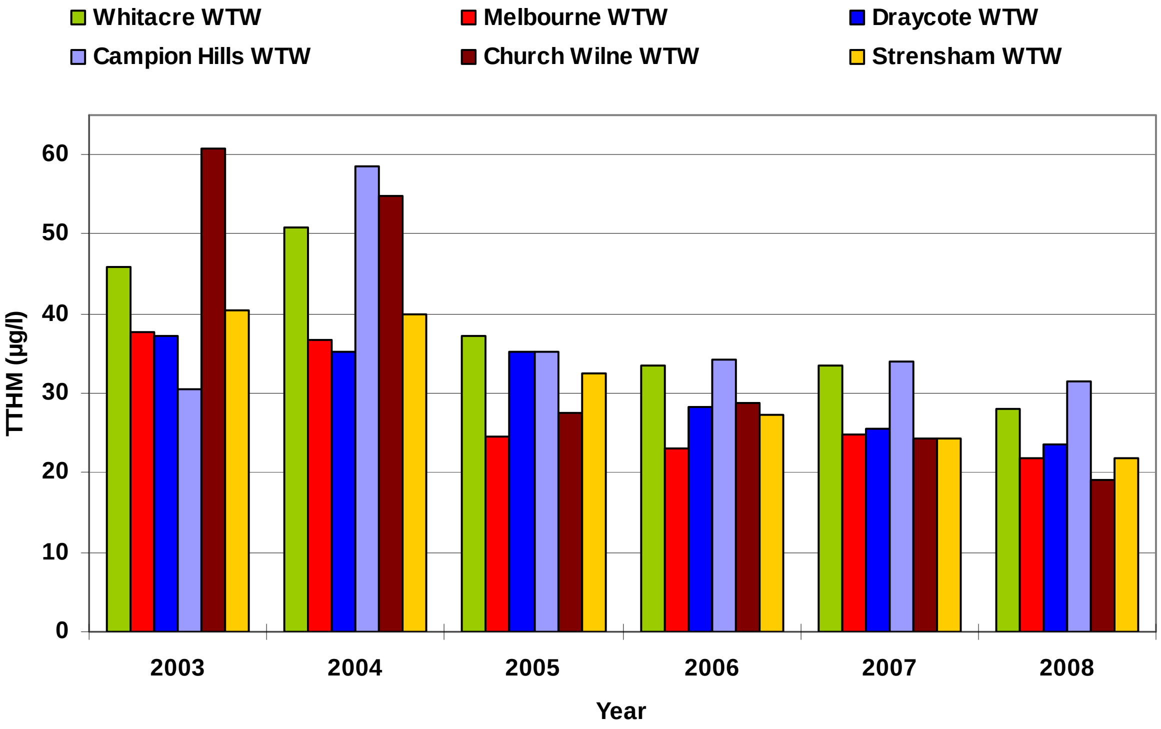


Figure 4.55; Annual average TTHM concentrations at each of the six WTW final waters between 2003 and 2008.

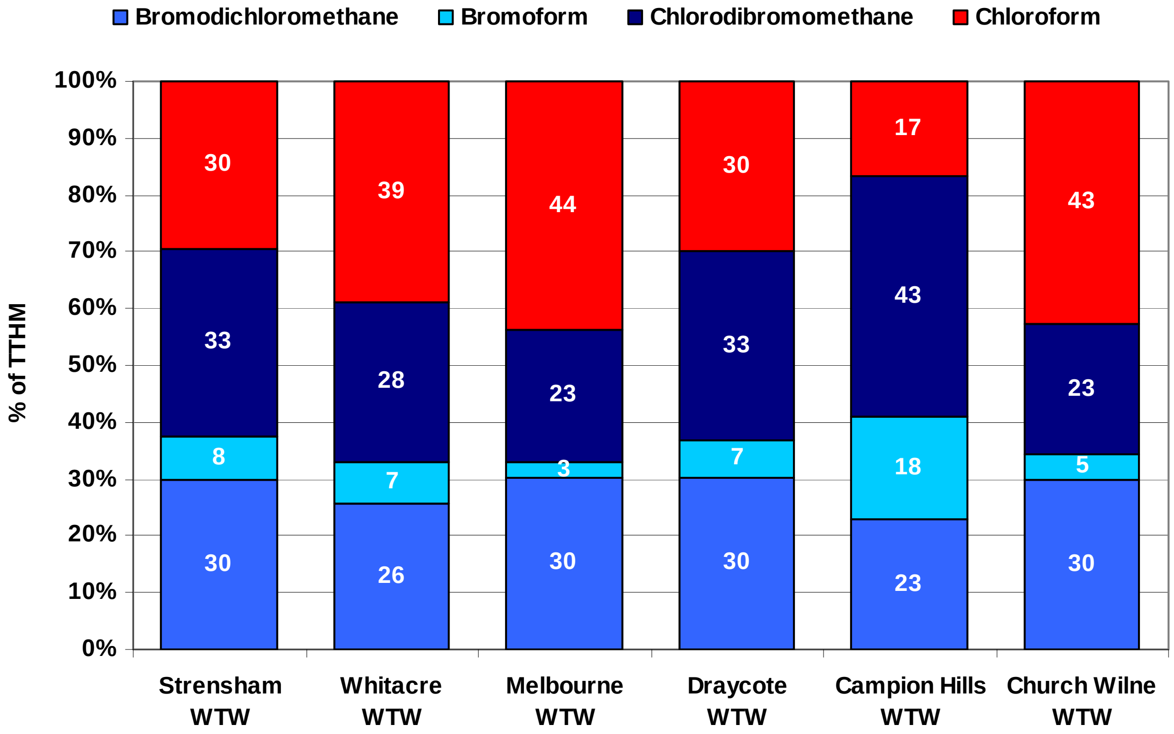


Figure 4.56; Four main THMs as a % of TTHM ~ based on averages between 2003 – 2008 at each of the WTWs final waters.

Chapter 5 Chlorine Decay

5.1 Introduction

The temporal and seasonal differences in raw water quality entering the six WTWs, along with the variation in the subsequent treatment and supply practices, were shown in the preceding chapter to have a considerable effect on the condition of the water arriving at the customer tap. This chapter investigates the influence of these changes specifically on chlorine decay through a combination of sampling programs and experimental results through each of the WTWs and distribution systems. The principal factors responsible for chlorine decay are investigated and a procedure for modelling it is outlined and its implications discussed.

The work in this chapter focuses on objective (ii) from Chapter 1;

- ***To investigate the influence of water quality parameters, initial chlorine concentration, temperature, contact time, water treatment unit and supply processes on chlorine decay, in order to develop empirically based models to relate functional dependencies.***

5.2 Test details

Chlorine decay was investigated through each of the six WTWs and their respective distribution systems via a series of co-ordinated sampling campaigns and concurrent laboratory tests. Bulk chlorine decay tests were conducted under both ambient and laboratory conditions designed to simulate operational conditions. The same sampling procedures and series of test conditions were applied to water from each of the six WTWs to facilitate cross comparison between WTWs and also between sampling days at the same WTW.

The tests were conducted in conjunction with spot samples through the WTWs and distribution systems (detailed in chapter 4), as well as various THM and bromide samples taken at explicit time intervals through the tests (which are reported in subsequent chapters).

Tests to determine the influence of temperature, TOC, bromide and initial chlorine concentration (C_0) on the bulk chlorine demand were undertaken at the Public Health Laboratory (PHL) at the UoB on water sampled immediately downstream of the GAC treatment stage (*i.e.* immediately upstream of disinfection). This location was selected, as since the suspension of pre-chlorination at each of the studied WTWs, the contact tank is the first chlorination point at each of the WTWs, and significant chlorine consumption and THM formation was observed to take place across this unit process (section 4.4).

A series of bulk decay tests, conducted over a longer 24-hour time period at ambient temperature and initial chlorine concentrations, were also performed on samples from the final waters and selected points within each of the distribution systems, to allow for a spatial and temporal representation of chlorine decay in the bulk phase in distribution. These were used in combination with specific or inferred knowledge of pipe characteristics to determine wall decay coefficients in accordance with the methodology described in section 3.2.2.

In a similar approach to Chapter 4, the majority of this chapter will concentrate on Strensham WTW, where additional samples and analysis allowed for a more comprehensive understanding to be formed. It is anticipated that the knowledge gained will be directly applicable to the other WTWs studied as part of this investigation, along with providing a useful and robust methodology that is applicable to any WTW in future investigations.

An outline summary of the tests undertaken at each of the sites is given in section 3.2.3. Each of the bulk decay tests were conducted in accordance with the methodology detailed in section 3.2.1.

5.3 Differences with cited literature

Although numerous previous studies have investigated chlorine decay (Wei *et al.*, 1974; Biswas & Clark, 1993; Clark *et al.*, 1994a; Beatty *et al.*, 1996; Vasconcelos *et al.*, 1997; Powell, 1998; Vieira *et al.*, 2004; Warton *et al.*, 2006), no standard procedure exists for conducting bulk decay tests. This study follows a slightly amended procedure used in previous work (Powell *et al.*, 1999; Hallam *et al.*, 1999). As the majority of this previous work concentrated on distribution system waters, the chlorinated samples were allowed to rest for a period of 15 minutes prior to taking the first chlorine measurement. It was argued that this approach would give homogeneity of chlorine within the sample, and should give realistic results, as the majority of the water in distribution was in excess of one hour old (Hallam, 1999; Hallam *et al*., 2001).

Courtis (2003) amended this procedure by taking the first of his samples after an initial mixing of the post-GAC sample water upon chlorination for one minute and letting this represent C_0. However, this approach meant a substantial amount of the total chlorine consumed in reactions was ignored which, when investigating THM formation, is important.

In this study, in a development and improvement on previous work, the water was dosed to a known C_0, stirred for one minute and then decanted into the amber glass bottles. The start of the test was taken as the time of chlorine addition to the water and the C_0 as the dose applied. The initial chlorine concentration was confirmed in each case by dosing equivalent volumes of distilled water.

Unlike previous studies at STW WTWs (Powell, 1998; Hallam, 1999; Hua, 2000; Courtis, 2003), this study observes chlorine decay in the WTW and distribution system where pre-chlorination has been phased out. Many previous studies (*e.g.* Haas and Karra, 1984; Gang *et al*., 2003b; Chang *et al*., 2006) also investigated chlorine decay where the water was dosed with chlorine concentrations well in excess of the chlorine concentrations typically observed under UK operational conditions. The present study concentrates on waters from both the WTW and distribution system, where tests were conducted with specific emphasis placed on replicating typical operational conditions to allow for modelling and simulation purposes. Where chlorine was already present in the water, tests were conducted at ambient conditions for reasons of practicality.

The majority of previous studies have investigated chlorine decay exclusively at either the WTW (Gallard & Gunten, 2002; Gang *et al*, 2003b; Kim & Yu, 2005) or the distribution system (Biswas *et al*., 1993; Kiene *et al*., 1998; Warton *et al*., 2006; Al-Jasser, 2007). This present study extends and improves upon that approach as it aims to provide an understanding of the change and variation of chlorine kinetics and influencing factors from the raw water to customer tap. Findings from six different WTWs and water supply systems are presented, thereby allowing for cross-analysis between a range of different operational treatment practices and potential source water quality characteristics.

5.4 Quantifying chlorine decay

Chlorine is a strong oxidizing agent that readily reacts with a variety of organic and inorganic material in the water and also with the material and accumulated material at the interface of treatment and supply equipment. The composition of these components in most cases remains unknown, with each observing different reaction mechanisms and kinetics with chlorine, with some reacting more rapidly than others. Due to the reactants being present in different concentrations with a variety of potential reactivities, the consumption of chlorine is a gradual process that occurs through complex sequential and parallel reaction pathways. Typically, chlorine decay in natural waters can be characterised simplistically by concurrent fast and slow reactions corresponding to steep and shallower declines respectively in the gradient of the profile of chlorine with time (as shown in the examples of free chlorine profiles for different unit processes from a sampling day at Strensham WTW in Figure 5.1).

The rates of these multiple reaction pathways are generally unknown (Deborde & von Gunten, 2008) and it would be impractical to model each separately. Consequently, all proposed decay mechanisms are inevitably simplifications, where the kinetics of chlorine decay are established empirically or semi-empirically. The first-order decay model is the simplest and most widely adopted empirical model, in which the chlorine concentration decreases exponentially with time (Zhang *et al*., 1992; Rossman *et al*., 1994; Powell, 1998; Hua, 1999; Chang *et al*., 2006). A law of this kind means that the rate of the reaction is proportional to the concentration of the reactant, the constant of proportionality being the decay constant 'K_B' in the following equations (Vieira *et al*., 2004):

$$\frac{dC}{dt} = -K_B.C \qquad (5.1)$$

Or: $$C = C_0 \, . \, \exp(-K_B.t) \qquad (5.2)$$

First order models have been successfully applied for chlorine decay in a range of waters, most of which were treated (Wable *et al*., 1991; Biswas *et al*., 1993; Rossman *et al*., 1994; Powell, 1998; Elshorbagy *et al*., 2000). Due to the majority of fast reactants being consumed across the contact tank at WTWs, bulk chlorine decay in distribution is considerably steadier and more stable than at the WTW. This allows for a first order relationship to be fitted to the data with a high degree of accuracy, with R^2 values usually greater than 0.9 (*e.g.* Figure 5.2). However, when studying chlorine decay at points of primary chlorination (*e.g.* through WTWs), fitting a first order relationship is complicated by the quick reactions that occur in the initial stages upon chlorination between chlorine and fast reacting organic and inorganic compounds in the water. These are highlighted by the initial steep gradient of the free chlorine profiles in the untreated or partially treated waters in Figure 5.1.

Figure 5.3 shows an example of the fundamental flaw to the fitting of a first order linear line to the chlorine decay in primary chlorinated water. The best-fit linear trend line (the gradient of which identifies the bulk decay constant, K_B, in equation 5.1) can be seen to under-predict C_0 in comparison to the actual C_0. In the example shown, the predicted C_0 is 1.41 mg/l; 0.29 mg/l below the actual C_0 of 1.7 mg/l. Applying the calculated bulk decay constant (0.46 l/hr), in a predictive model with a C_0 of 1.7 mg/l, the model yields predicted chlorine concentrations which are appreciably higher than the observed concentrations (Figure 5.4).

For a preliminary comparative analysis of the reactivity of different waters, a first-order model over the entire measured decay period is usually acceptable due to its ease of application and cost effectiveness (see section 5.5). However, as a means of modelling chlorine concentrations with time, the first order approach is not suitable for waters where first chlorination takes place, due to the associated problems with the differences in fast and slow reactant kinetics (as preceding plots have demonstrated).

The problems associated with modelling the rapid initial and prolonged slower decay of chlorine has been observed by several authors in previous studies (Qualls & Johnson, 1983; Jadas-Hécart *et al*., 1992; Zhang *et al*., 1992; Vasconcelos *et al*., 1997; Gang *et al*., 2003; Vieira *et al*., 2004) and has been modelled in a range of ways of varying complexities for different types of waters, over a variety of time periods to represent different stages in the reactions (see section 2.5). These studies were conducted on different types of waters ranging from raw and final waters to laboratory-derived waters, treated under a variety of treatment practices and conditions, each displaying different reaction kinetics. For this study, primary consideration was given to the feasibility of modelling chlorine decay in a way that could be readily adaptable to other WTWs in a cost-effective manner. To address this aim, a two-stage approach to modelling chlorine decay in primary chlorinated water is explored. Justification is provided and the effects of independent parameters explored (see section 5.6).

5.5 Changing reactivity through the WTW

The consumption of chlorine and the formation of DBPs at the WTW are influenced by both the raw water constituents and the subsequent treatment practices adopted. Laboratory-based bulk decay tests (over two-hour periods at the same initial chlorine concentration and temperature) were performed on water sampled from the raw, post-clarifier, post-RGF and post-GAC stages, to allow for an introductory insight into the effects of each to be quantified. Summaries of first order bulk decay constants over 1-hour and 2-hours are shown in Figure 5.5 and 5.6, respectively.

It is evident that the 1-hour bulk decay constants were always higher than the associated 2-hour bulk decay constants, an aspect that will be discussed in more detail in section 5.6.1. It is also apparent that as successive treatment processes remove cumulatively increasing amounts of the water’s potentially reactive organic and inorganic material, there was a corresponding decrease in the amount of chlorine consumed and the pertinent bulk decay constants. For example, 2-hour bulk decay constants decrease from an average of 1.73 l/hr in the raw water, to 0.15 l/hr in post-GAC samples. As with the decline in TOC concentrations through the

WTW (Figure 4.15), the main reduction occurs due to the clarification process, with an average percentage decline in raw water bulk decay constants (over 2 hours) of approximately 78 %. Further reductions in average raw water bulk decay constants over the RGF and GAC unit processes account for considerably smaller declines of approximately 5 % and 7 %, respectively (Figure 5.7).

Correlation between all sampling points bulk decay constants and concurrent TOC concentrations shows a positive relationship (R^2 ~ 0.46, significant at the 1 % level over 2-hours) (Figure 5.8). Broken down to individual sampling locations the positive relationship becomes more robust with successive treatment processes through the WTW (Figure 5.9). No significant relationship was observed at the raw water sampling point, whereas at the post-GAC stage (R^2 ~ 0.69, significant at the 1 % level), the relationship is noticeably stronger compared to the post-RGF and post-clarifier points, with R^2 values of 0.50 (significant at the 5 % level) and 0.23 (significant at the 15 % level), respectively.

TOC is only a surrogate measure of the organic compound inventory in a given water and can therefore only be used as an estimate of the overall reactive power. The chemical matrix of the water will contain a myriad of fast and slow reactants that are highly unlikely to remain in steady proportions through the treatment processes. The increasing strength of relationship between bulk decay constants and TOC is likely to be a result of the removal of fast reacting material (both organic and inorganic), which leads to the effects of the slower reacting organic and inorganic fraction increasing in prominence with time, thus emphasising the relationships portrayed. This was also demonstrated in the increasing stability of bulk decay constants through the WTW between sampling days (Figures 5.5 & 5.6), and highlights the problems with using raw water (as in previous studies laboratory tests) to develop predictive chlorine decay models at WTWs and distribution systems (Powell, 1998; Hallam, 1999; Hua, 2000).

5.6 Empirical modelling of chlorine decay

Determination of decay constants by laboratory based testing is useful as a reference method, but is also time consuming, expensive, and impractical on a routine operational basis. Mathematical relationships between bulk decay constants and the factors affecting them, would be of aid in obtaining those coefficients in a more expeditious way that could utilise water quality data already collected in routine monitoring programs (Vieira *et al.*, 2004). This section explores such relationships, based principally on chlorine decay across the contact tank as this is currently the first point of chlorination in each of the investigated WTWs, and has been shown to be where significant differences in chlorine consumption resulted from changes in source water characteristics and operational practices.

5.6.1 Characterising the temporal variation in chlorine decay

As described in section 5.4, the decay of chlorine in natural waters that are chlorinated for the first time can be characterised by fast and slow reactions that are dictated by a water's characteristics and the prevailing chlorination conditions. Observations from the tests on post-GAC water (described in section 5.6.2) showed that the majority of quick reactions with chlorine occurred within the initial five-minute period when, due to logistical reasons explained in section 3.2.1, the first chlorine measurements were taken. Between 9 and 28 %

(average ~ 19 %) of the initial chlorine was consumed within this period. As described in section 2.6, this initial decay is strongly influenced by chlorine's reactions with inorganic substances in a reduced valence state such as iron, manganese, sulphide, bromide and ammonia.

Analysis showed that with the omission of the first five-minutes of the test period, a first order fit to the data was significantly improved (*e.g.* Figure 5.10). The average R^2 value of fitted linear trend lines to each of the post-GAC test data at Strensham WTW increased from 0.69 to 0.91 (for trend lines including, and not including, the initial five-minutes, respectively). Indeed, a first order relationship can be seen to model chlorine decay more accurately with the omission of greater lengths of time from the start of the test, as the relationship avoids more of the rapid initial reactions (Figure 5.11). However, the increases in R^2 values, or the improvements in accuracy of the first order fit, are seen to diminish with the omission of greater lengths of time from the start of the test. Whereas the average R^2 value increased by 31 % (from 0.69 to 0.91) when the initial five minutes is omitted in the fitting of the first order trend line, the omission of a further five minutes only results in a further 2 % increase in the average R^2 value (from 0.91 to 0.93) (see Table 5.1).

To facilitate practical modelling and simplified applicability to alternative WTW, a two-stage modelling process is proposed. In the first stage the initial drop in free chlorine over the first five minutes is modelled via a percentage drop in the initial free chlorine concentration (C_0):

$$C_{5mins} = C_0 - (p.C_0) \tag{5.3}$$

Where: C_{5mins} = Free chlorine concentration at five minutes (mg/l)

C_0 = Initial chlorine concentration at zero minutes (mg/l)

p = Factor determined by experimentation

The resultant concentration can then be used as the initial chlorine concentration in the latter stage, where the chlorine decay is modelled via first order kinetics, according to equation 5.2 (where C_0 is represented by C_{5mins}), which has one unknown, K_B.

A conventional means of determining the bulk decay constant (K_B in equation 5.2) involves calculating the gradient of a best-fit linear trend line through data in a ln(C) versus time plot. For a rigorous assessment of this value, the line is constrained through the initial chlorine concentration (in this case, C_{5mins}). This leads to one constant in the equation of the line (*i.e.* the K_B value), thus making subsequent application in calculating chlorine concentrations with time more straightforward. An example of this approach is shown by the red line in Figure 5.12. Due to the characteristic slightly concave profile of chlorine decay, particularly for the smaller time values, the accuracy of the fit of this line is shown to improve when the best-fit line is not constrained through C_{5mins} (shown by the blue line). In addition to lowering the K_B value, this approach leads to the introduction of a further constant (ΔC_i), shown in Figure 5.11, as the difference between $\ln(C_{5mins})$ and the y-intercept of the blue line. In terms of the free chlorine concentration represented by ΔC_i, the difference is minimal in the example shown (0.024 mg/l).

In similar calculations for all tests across the six WTWs an average difference of 0.027 mg/l was observed. Taking into consideration the amplified sampling errors and temporal changes in the reactivity of the water in the initial stages of chlorination, this difference is relatively small in comparison to the improvement in the accuracy of the best fit trend lines to the data. R^2 values increased from an average of 0.83 for the lines constrained through C_{5mins} to 0.92 for the lines not constrained through this point.

Given the improvement in the accuracy of K_B values and the additional complications in incorporating the functionality of ΔC_i with independent parameters (*e.g.* temperature) in the modelling procedure, ΔC_i is assumed for the remainder of the chapter to be negligible. Calculations of all bulk decay constants in the post-five minute period are made using the unconstrained line method. Further justification for this approach will be demonstrated in section 5.8.

A further complication to both the reporting and the application of chlorine decay models is the time period for which decay constants are calculated. Figure 5.13 shows two examples of the decline in the bulk decay constant with an increase in the fitting time used in their calculation. The faster reactions that occur in the initial stages of chlorination are represented by the higher bulk decay constants, and steep gradient of the curve in the preliminary stages, after which the curve flattens and bulk decay constants become progressively more stable.

The bulk decay constant is therefore visibly dependant on fitting time and is clearly not constant, showing that the first order relationship is not appropriate for situations where reactants with vastly different reaction kinetics are present in the water. The use of a second, or higher order equation leads to the need to define the functional dependence of one or more coefficients on various independent parameters such as temperature, C_0, Br and organics concentration. These models have been tested and evaluated for their accuracy, reliability and durability (Haas & Karra, 1984; AWWARF, 1996; Powell, 1998; Hua, 1999; Hallam, 2000; Vieira *et al*., 2004) with conflicting reports. Potentially these approaches could provide a more accurate representation of chlorine decay, as the more adjustable parameters a model has, the wider the range of decay profiles it can accommodate. However, they are time consuming and costly to operate on an operational basis to which this work is primarily targeted.

Although the concept of the bulk decay constant is seen to be inconsistent with the fitting time used to calculate them, it is deemed that for predictive purposes, a first order approach is justified for contact tank time scales of the order of an hour, where the gradient of the curves (*e.g.* in Figure 5.13) is considerably less than for shorter times. This approach comes with the imperative caveat that the application of a given bulk decay constant is limited to a specified time interval centred around the fitting time originally used for its calculation. This will be discussed further in section 5.6.3.

5.6.2 Variation of bulk decay rate with independent parameters

Variation in bulk decay rates can be a result of several different parameters, and initial chlorine concentration, TOC concentration, temperature and pH are known to have a significant impact. Preliminary tests suggested that trying to find a holistic relationship between the above parameters and chlorine decay in combination would be difficult, due to the problems associated with isolating influences from independent factors. Therefore, under carefully controlled laboratory conditions, a series of tests was conducted on post-GAC water to identify the relationships between bulk decay and each parameter separately, while other parameters remained steady (as detailed in section 3.2.3). To facilitate the development of two-stage modelling of chlorine decay, the results in the proceeding sections are described according to the two different stages.

Initial chlorine concentration (C_0) The resultant bulk decay constants observed with the variation of C_0 on post-GAC water suggested an inverse relationship (Figure 5.14), with a power fit giving an accurate portrayal of observed results (R^2 values of 0.88 for 5-60 minute and 0.79 for 5-120 minute results, both significant at the 1 % level). Although the tests were not all from the same sampling day, there were only relatively small variations in TOC (average ~ 2.36 mg/l, s.d. ~ 0.33 mg/l) and bromide (average ~ 51.4, s.d. ~ 14.1 µg/l) concentrations, and temperature was the same between tests (15 °C).

UKWIR (1998) and Hallam (1999) suggested that a possible mechanism to explain the inverse relationship between bulk decay and C_0 is that the number of reactive sites (or reactants) varies as a function of the initial chlorine dose. At low doses, chlorine may be expected to react primarily with the most reactive sites and decay will be rapid, resulting in high bulk decay constants. However, if the dose is higher, chlorine will be available to react not only with the most reactive but also the slower reactants, hence reducing the overall decay constant.

The percentage decline in chlorine concentrations over the initial five minutes was also inversely related to the initial chlorine concentration, decreasing from approximately 50 % of

C_0 at the lower initial chlorine concentrations to 15 % at the higher concentrations (Figure 5.15).

Temperature (Θ) The rate of most chemical reactions increases with temperature. The annual variation of water temperature (Figure 4.14) was seen to vary between 4 and 25 ^{o}C at Strensham WTW and was observed to have significant effects on both chlorine consumption and THM formation. A positive relationship was observed between bulk decay constants and temperature on each of the summer 2007 sampling days on Strensham post-GAC water (Figure 5.16). In each case the bulk chlorine decay constant saw an approximate two-fold increase with the rise in temperature from 5 ^{o}C to 25 ^{o}C. This is significantly lower than the anticipated quadrupling of bulk decay rates predicted by the approximate rule (described in section 2.6.3) by Fair (1965), which stated reaction rates double for every 10°C rise in temperature. The percentage decline and the actual amounts of chlorine consumed in the initial 5-minute period also increase with temperature in a similar fashion (Figure 5.17).

Organics concentration (TOC) For most waters, the reactions of chlorine with organic matter make up the majority of the chlorine demand (Clark & Bouton, 1998). TOC is the most common surrogate measure of organic material in water, and it is to be expected that a relationship would exist between this parameter and the rate of chlorine decay. Indeed, previous research (AWWARF, 1996; Powell, 1998; Hallam, 1999; Hua, 2000; Courtis, 2003; Vieira *et al.*, 2004) has shown that such a relationship does exist, with a higher concentration of TOC being associated with higher bulk decay constants.

The work by AWWARF (1996) and Powell (1998) suggested a linear relationship between the TOC concentration and the chlorine bulk decay rate. Hallam (1999) and Hua (2000) found in their work using dilutions of raw water that a linear relationship did not accurately represent bulk decay at low concentrations of TOC. They both proposed the use of a power function (equation 2.12), where both the TOC concentration and bulk decay constant tend towards zero as the number of potential reactant molecules in the water decreases.

Figure 5.18 shows that such a power relationship fits the data for all bulk decay tests on post-GAC water reasonably well (R^2 value of 0.85, significant at the 1 % level), considering that tests were carried out at different times of the year and it is likely that the chemical matrix of the water will change temporally.

Bromide (Br) As explained in Chapter 4, the relationship between bromide and other natural and anthropogenic constituents in the water (such as organic compounds and chlorine) is complex and will have a profound influence on the amount of THM formed. Bromide was seen to have an inverse relationship on bulk decay rates at Strensham WTW (Figure 5.19), although the relationship was weak (R^2 values of 0.31 and 0.51 over 1 and 2 hours respectively, significant at the 15 and 10 % levels). It is likely that an increase in the bromide concentration would, via the stronger bromide / chlorine ratio, lead to the importance of chlorine in the numerous reactions taking place in the water decreasing, subsequently leading to the observed decline of bulk decay constants. The percentage decline and the amount of chlorine consumed in the initial five-minute period were also seen to decrease with increasing bromide concentrations (Figure 5.20).

Sample water dilution As many treated or partially treated waters have to adhere to either stringent water quality standards or other operational limits, samples taken at the WTWs are often reflected by water quality parameters where measures or concentrations often lie within a narrow band with little variation. Therefore, the influence of their variation on chlorine decay is difficult to assess, without the aid of numerous, costly samples at different times of the year.

Previous studies have shown the use sample water dilution to be a useful approximation to the change in reactivity observed with independent parameters (Hallam, 1999; Hua, 2000; Courtis, 2003). Although it is accepted that it is not ideal, due to the uncertainty of what fraction of the organic and inorganic matrix is being replaced, this approach was adopted on each of the sampling days, with sample water diluted to 1:2 and 2:1 parts with distilled water, and identical bulk decay tests conducted.

The samples at Strensham showed that the dilution data fitted relatively well with similar observed TOC concentrations. The trend lines fitted solely through the sample water dilution tests shown in Figure 5.18 show close proximity in distance and gradient to the trend lines for all TOC versus bulk decay constant data, indicating that the dilution method is a suitable approximation for the change in bulk decay constants with organics concentration in this case.

As would be expected the percentage decline and the actual amount of chlorine consumed in the initial five-minute period also increased with sample water strength through dilution (Figure 5.21).

5.6.3 Empirical equations

The data from all the tests on post-GAC water were collated using the stepwise regression function of the statistical analysis package, SPSS (Statistical Package for Social Scientists), to develop an equation for the bulk decay constant, K_B, of the form shown in Equation 5.4. In stepwise regressions, decisions about the order in which predictors are entered into the model are based on a purely mathematical criterion, according to the selection method applied. In this study the forward selection method was chosen in SPSS. This involves starting with no variables in the model, trying out the variables one by one and including them if they are statistically significant. Each time a predictor is added to the equation, a removal test is made of the least useful predictor (Field, 2005).

$$K_B = A + (a \cdot C_0) + (b \cdot \Theta) + (c \cdot TOC) + (d \cdot Br) \quad (5.4)$$

Where: C_0 = Initial chlorine concentration (mg/l).

Θ = Temperature (^oC).

Br = Bromide (µg/l)

A, a, b, c, d = Constants determined by stepwise regression.

Given the dependence of the bulk decay constant on the fitting time (described in section 5.6.1), the stepwise regression procedure was applied to develop equations for four different time periods; 5-30, 5-60, 5-90 and 5-120 minutes. These will be applied in subsequent modelling work to account for differences in retention time across contact tanks (Chapter 7). An equation of form displayed in equation 5.4 was also developed (using the same stepwise regression procedure) to determine a factor (p in equation 5.3) to represent the percentage decline over the initial five-minute period in the first of the two stage modelling process.

Table 5.2 details the constants (from equation 5.4) determined through this method for each of the six WTWs. Figures 5.22 and 5.23 show that for the four predetermined time periods at Strensham WTW, the observed bulk decay constants correlate well with the bulk decay constants predicted via the equations applied for each of the corresponding test conditions. A better fit of the data to the 45º line was observed for longer time periods. The greater scatter of data for the shorter 5-30 minute time period and also in the observed versus predicted factor drop in C_0 (Figure 5.24), once again represents the variability in both magnitude, and across test conditions, of the initial rapid reactions. It also signifies the greater inaccuracies with taking chlorine measurements over shorter time periods where sampling and timing errors are further amplified. The use of a colorimetric method to determine chlorine concentrations exemplifies this problem due to the time required to conduct measurements. With hindsight, the use of an alternative measurement technique (such as an online amperometric instrument) would perhaps have been more suitable, particularly for representation of the early stages of tests conducted on first chlorinated waters.

5.6.4 Performance of equations

To test the feasibility of the two-stage approach, the equations were applied in sequence to predict chlorine concentrations with time (over 1- and 2-hour periods). A typical example of this is shown in Figure 5.25 for a summer 2007 sampling test conducted under the conditions of an initial chlorine concentration of 1.7 mg/l, temperature of 15 °C and no sample water dilution.

Plots showing predicted versus observed chlorine concentrations at 5, 60 and 120 minutes are shown in Figures 5.21, 5.22 and 5.23, respectively. On the whole, chlorine concentrations were satisfactorily modelled across the range of tests with concentrations approximately ± 0.05 mg/l (± 4.2 %) from the observed concentrations after 60 minutes and ± 0.1 mg/l (± 6.5 %) after 120 minutes. The scatter of data points correlates well with the 45° line implying good fit between predicted and observed data, although the relationship gets worse with time.

5.7 Distribution system

Upon completion of the physical and chemical treatment processes that purify the raw water to make it potable, the final water is either pumped or gravitates into the distribution system with a small residual free chlorine concentration (at Strensham WTW this averaged 0.44 mg/l between 2003 and 2008, s.d ~ 0.04 mg/l). This residual will gradually decay within the distribution system and, if it is not properly managed, microbiological and bacteriological growth may occur, particularly towards the extremities of a system.

Chlorine decay in distribution systems is generally considered to consist of two components; bulk decay and wall decay (Clark, *et al*. 1993a). The two decay mechanisms are generally considered separately, with the overall decay constant taken as the sum of the two separate parts;

$$K_T = K_B + K_W \tag{2.19}$$

Where:

K_T = Overall chlorine decay constant (l/hr)

K_B = Bulk decay constant (l/hr)

K_W = Wall decay constant (l/hr)

5.7.1 Bulk chlorine decay

As the majority of fast reactants have had the time to react with chlorine through the WTW, first order decay approximations are appropriate to model chlorine decay in the distribution system, with R^2 values ranging between 0.90 and 0.99, with an average of 0.95, all significant at the 1 % level (Tables 5.3 and 5.4). This is in accordance with previous research where successful application of first order models have been demonstrated (Hallam, 1999; Powell *et al*., 2000; Al-Jasser, 2007).

The bulk decay constant will fall as the water is conveyed through the distribution system and the amount of reactive material decreases. This is generally the case between the final water and Oversley Green BPS outlet; however, the effect is not so apparent between Oversley Green BPS outlet and Tysoe DSR outlet water (Figure 5.29) with the observed bulk decay constants on some occasions increasing by small amounts (the order of 0.01 l/hr) between the two points. This variation can be attributed to the differences between sampling days of several interfering factors including, *inter alia*, the differences in chlorine concentration, TOC concentration, previous re-chlorination history and flow conditions (*e.g.* diurnal and seasonal variation in supply and demand characteristics).

Average bulk decay constants over 24-hours fall by approximately 50 % from 0.051 l/hr at the final water to 0.027 l/hr at the outlet to Oversley Green BPS outlet, immediately after the first re-chlorination point in the distribution system. Between the latter and Tysoe DSR (0.023 l/hr average), the smaller decline can be attributed to a reduction in the remaining slow reactants.

As the tests were conducted at a range of ambient conditions it is difficult to discern any palpable relationships between bulk decay constants and individual water quality parameters. Final water TOC concentrations were fairly consistent between sampling days in comparison to samples taken at preceding sampling points through the WTW (due in part to set treatment targets water leaving the WTW), ranging between 1.33 and 2.91 mg/l with a standard deviation of 0.38 mg/l. This low variation is reflected in the weak correlation with bulk decay constants, especially over 24-hours (Figure 5.30).

A positive linear relationship of the bulk decay constant with temperature is more evident at the final water ($R^2 \sim 0.69$), Oversley Green BPS outlet ($R^2 \sim 0.80$) and at Tysoe DSR outlet ($R^2 \sim 0.81$). A doubling of temperature from 10 ^oC to 20 ^oC leads approximately to a 50 % increase in the bulk decay constants at these points (Figure 5.31). No significant relationships were observed between bulk decay constants and initial chlorine concentration and bromide concentrations. This is to be expected as chlorine and bromide concentrations are low in a low reactivity water.

5.7.2 Wall chlorine decay

At the WTW the effects of wall decay at the surface of pipes and treatment processes can largely be ignored due to the relatively small wall surface area compared to the volume of water contained. In contrast, in pipes and certain distribution system apparatus (*e.g.* BPS and valve fittings), wall decay of chlorine may feature prominently. Research by Clark *et al.* (1993) showed that bulk decay accounted for between 2 and 73 % of the in situ chlorine decay in distribution systems dependant on pipe material and over 96 % within DSRs. Woolschlager & Soucie (2003) showed that an average of 23 % of the free chlorine loss could be attributed to wall reactions with concrete pipes, whereas Hallam (2000) showed the ratio of K_B to K_W ranged from 0.1 to 40, dependant on pipe and water characteristics. Wall decay, which includes reactions with the wall material itself, with adhering biofilms and with accumulated sediments, is mostly a function of pipe characteristics: material, inner coating, age, diameter and presence of attached biofilms (Hallam, *et al*., 2002; Vieira *et al*., 2004; Gibbs *et al*., 2006).

The measurement of wall decay is inherently complex and is also difficult to influence, as capital investment would be required to refurbish or renew pipes, pumps or storage facilities in the distribution system. For the purposes of this study an assessment of the effects of wall decay in certain stretches of distribution was made via the combination of knowledge obtained from the bulk decay tests, with spot samples taken at the start and end of pipes, according to the methodology provided in section 3.2.2. Where data were found to be insufficient and unfeasible to obtain, estimates were made according to previous UoB studies and literature (*e.g.* Hallam, 1999; Courtis, 2003) appropriate to the characteristics of pipe being considered. Their subsequent use in the modelling of chlorine decay will be discussed in more detail in Chapter 7. As with bulk chlorine decay, the accuracy of each of the estimates could be improved through the use of more tests under a wider range of conditions.

5.8 Inter-comparison of 6 WTW and parts of their distribution systems

Although conducted to a lesser extent, the tests at the five remaining WTWs and their associated distribution systems provide an insight into the changing reactivity of each of the WTW's waters under a range of comparable test conditions between WTWs.

Raw water bulk decay tests, each conducted at an initial chlorine concentration of 1.7 mg/l and a temperature of 15 ºC (Figure 5.32), showed each of the WTW source waters to be highly reactive, particularly in the initial stages post chlorination, where the average decline in chlorine concentrations over the first five-minutes was 1.03 mg/l. Bulk decay constants over 2-hours ranged between 0.7 and 1.46 l/hr (average ~ 1.12 hr^{-1}), with the most reactive source waters being at WTWs where raw water storage is small or absent, *e.g.* Whitacre, Campion Hills and Strensham WTWs.

The results of the variation in temperature, initial chlorine concentration and sample water dilution for tests conducted on post-GAC waters at each of the six WTWs are summarized in Figures 5.33 to 5.35 (once again with the omission of the first five-minutes of the tests, for reasons explained in section 5.6.1).

An inverse relationship between initial chlorine concentration and bulk decay constants was again observed on most of the sampling days, with the average bulk decay constants (between 5-60 minutes) decreasing by 35% and 20 %, between 1.3 – 1.7 mg/l and 1.7 – 2.1 mg/l, respectively. Similarly, for bulk decay constants between 5-120 minutes there was an increase of 28 % and 23 % over the same changes in chlorine concentration.

Temperature can be seen to have a significant positive relationship, with the average bulk decay constants (between 5-60 minutes) increasing by 24 % and 58 %, between 5 ºC – 15 ºC and 15 ºC – 25 ºC respectively. Similarly between 5-120 minutes there was an increase of 36 % and 53 % over the same changes in temperature.

Predictably, bulk decay constants at each of the six WTWs are seen to decrease by approximately a factor of two with the dilution of the sample water from 1:0 to 2:1 and from 2:1 to 1:2 (sample water {SW} : distilled water {DW}). A positive relationship between bulk decay constants and corresponding TOC concentrations for all tests conducted on each of the six WTWs post-GAC waters at 1.7 mg/l and 15 $^{\circ}$C is demonstrated in Figure 5.36. Bromide was seen to have the reverse effect on chlorine bulk decay rates (Figure 5.37), although a strong relationship was difficult to discern across all of the six WTWs tests (R^2 ~ 0.17 / 0.18, significant at the 5 % level), due to the differences in other water quality parameters.

Due in part to the variation in the efficiency of organics removal through each of the six WTWs (section 4.6), the WTWs with the most reactive raw waters do not necessarily have the most reactive post-GAC waters (Figure 5.38). On average across the six WTWs, there was an approximate 80 % reduction in bulk decay constants between the raw water and the post-GAC samples (based on tests between 0-120 minutes). Melbourne WTW, which exhibited some of the lowest organics removals across the WTW (Figure 4.50), also saw the lowest reductions in bulk decay constants between the raw and post-GAC samples (75 %), leading to a change from it having the least reactive water at the raw water, to having some of the most reactive by the post-GAC sampling point in comparison to other WTWs.

A summary of the differences between the reactivity of the water at the final waters of each of the six WTWs and a DSR towards the end of each of their respective distribution systems is shown in Figure 5.39. The wide range of ambient conditions again complicates comparison. Whitacre, Draycote and Melbourne WTWs, which exhibited some of the highest TOC concentrations measured on the sampling days at their final waters, also exhibited some of the highest bulk decay constants (particularly over the initial stages of the tests) (see Table 5.4 for a summary of bulk decay constants over 24 hours).

It was observed that the WTWs with some of the longest retention times in the distribution system also exhibited the largest difference between the bulk decay constants at the final water and the distribution site (Figure 5.39). This is expected due to the water passing through more chlorination points and having a longer time to react with chlorine before reaching the latter sampling point. Typically, therefore, only slow reactants remain in the water by the latter stages. The lowest bulk decay constants at the final water were observed at Campion Hills WTW where the samples were taken after the storage of the water in the final water service reservoir.

The data collected from the different bulk decay tests at each WTW were used to compile a set of equations for the calculation of the bulk decay constants (over 5-30, 5-60, 5-90 and 5-120 minutes) and a factor to represent the initial drop in C_0 over the initial five-minute period (as in section 5.6.3 for Strensham WTW). A smaller dataset in comparison to Strensham WTW was used to evaluate the equations. Further tests at a wider range of test conditions would naturally improve the accuracy of these equations. The results of the coefficients of these equations are shown in Table 5.2. The scatter plots showing the relationship between predicted values using these equations and the actual values observed in the tests are shown in Figures 5.40, 5.41 and 5.42. Correlation at each of the WTWs is satisfactory between observed and predicted values. As with Strensham the scatter is more dispersed around the 45° line for the initial five minute factors (p) compared to the second stage bulk decay constant values.

In a similar manner to that described in section 5.6.4, the predictive equations were used in sequence to predict temporal profiles of free chlorine concentrations. The scatter plots of predicted versus observed free chlorine concentrations at 5, 60 and 120 minutes are shown in Figures 5.43, 5.44 and 5.45, respectively. Similar to the analysis at Strensham WTW, the gradient and proximity of the linear trend line through all the data correspond pleasingly with the 45° line, indicating good predictive capabilities of the equations. The accuracy again declines with time, with the predicted concentrations after 120 minutes being generally under-predicted. The average difference between observed and predicted chlorine concentrations across the six WTWs decreased from 0.039 mg/l (2.9 %) after five minutes, to 0.047 mg/l (4.1 %) after one-hour, and 0.061 mg/l (6.7 %) after two-hours.

With reference to the method described in section 5.6.1, chlorine concentrations after 60 and 120 minutes were calculated using equations which collated the bulk decay constants determined by constraining the best fit lines through the $\ln(C_{5mins})$ value. The results are displayed in Figures 5.46 and 5.47, after 1 and 2 hours, respectively. In comparison to Figures 5.44 and 5.45, the corresponding results displayed in Figures 5.46 and 5.47, respectively (using the constrained method), show a weaker correlation between the observed and predicted concentrations, with the average difference between the predicted and observed being greater after 1-hour (at 0.059 mg/l, 5.14 %) and after two-hours (at 0.099 mg/l, 9.90 %). The higher calculated K_B values (and weaker accuracy in their determination) in the constrained method leads to the predicted chlorine consumption being greater than the observed concentrations, shown in the plots by the increasing distance of the linear trend line with time.

5.9 Conclusions

Strensham WTW and distribution system results

- Successive treatment processes through Strensham WTW led to a reduction in the water's reactivity with bulk decay constants reducing from 1.73 l/hr at the raw water to 0.15 l/hr at the post-GAC sampling point (over 2-hours) (Figure 5.6). The main reduction occurred due to the clarification process, with an average percentage reduction of approximately 75 % of raw concentrations.

- A first order model, although sufficient for an initial comparison of different waters reactivities, was shown to be inappropriate for modelling chlorine decay temporally, due primarily to the rapid reactions that occur in the early stages upon the first chlorination.

- With the omission of the first five minute period of the tests, the average R^2 value of fitted linear trend lines to each of the post-GAC test data at Strensham WTW increased from 0.69 to 0.91. Further extensions to the initial period of the tests were shown to not significantly improve accuracy.

- A two stage modelling process was proposed, where the initial 5-minute period of chlorine decay would be represented by a percentage drop in C_0 (calculated by applying a factor, *p*, to C_0), followed by first order modelling of the latter stage. This was deemed for predictive purposes to be suitable for contact tank time scales of the order of an hour.

- The first order bulk decay constant (K_B) was observed to vary with the initial chlorine concentration (C_0), TOC, bromide and temperature, to which K_B:

    - had an inverse relationship with C_0 and bromide;
    - had a positive power relationship with TOC;
    - had a positive relationship with temperature, where a twofold increase in K_B with the rise in temperature from 5 °C to 25 °C.

- Application of the two stage process to the range of test conditions showed encouraging results with concentrations approximately ± 0.05 mg/l (± 4.2 %) from the observed concentrations after 60 minutes and ± 0.1 mg/l (± 6.5 %) after 120 minutes.

- First order decay approximations were found to be more appropriate to model chlorine decay in the distribution system, with R^2 values for the fitted ln-linear trend lines ranging between 0.90 and 0.99, averaging 0.95. Average bulk decay constants fall by approximately 50 % from 0.051 l/hr at the final water to 0.027 l/hr immediately after the first re-chlorination at the outlet to Oversley Green BPS outlet. Bulk decay constants continue to decline through the distribution system, although at a diminishing rate.

- As the final water and distribution system tests were conducted at a range of ambient conditions it is difficult to discern any palpable relationships between bulk decay constants and individual water quality parameters. However, a positive linear relationship of the bulk decay constant with temperature is evident at the final water (R^2 ~ 0.69), Oversley Green BPS outlet (R^2 ~ 0.80) and at Tysoe DSR outlet (R^2 ~ 0.81). A doubling of temperature from 10 ^{o}C to 20 ^{o}C leads approximately to a 50 % increase in the bulk decay constants at these points (Figure 5.31).

Inter-comparison of 6 WTW and parts of their distribution systems

- Raw water bulk decay constants over 2-hours ranged between 0.7 and 1.46 l/hr (average ~ 1.12 l/hr) across the six WTWs, with the most reactive waters present at sites where raw water storage is small or non-existent, *e.g.* Whitacre, Campion Hills and Strensham WTWs.

- As at Strensham WTW, an inverse relationship between initial chlorine concentration and bulk decay constants was again observed on most of the sampling days at each of the WTWs, with the average bulk decay constants (between 5-60 minutes) decreasing by 35% and 20 %, between 1.3 – 1.7 mg/l and 1.7 – 2.1 mg/l, respectively. Similarly, for bulk decay constants between 5-120 minutes there was an increase of 28 % and 23 % over the same changes in chlorine concentration. Temperature can be seen to have a significant positive relationship, with the average bulk decay constants across the six WTWs (between 5-60 minutes) increasing by 24 % and 58 %, between 5 ºC – 15 ºC and 15 ºC – 25 ºC respectively. Similarly between 5-120 minutes there was an increase of 36 % and 53 % over the same changes in temperature. Predictably, bulk decay constants at each of the six WTWs are seen to decrease by approximately a factor of two with the dilution of the sample water from 1:0 to 2:1 and from 2:1 to 1:2 (sample water {SW} : distilled water {DW}).

- K_B (one and two hour values) variation with TOC and bromide could be represented by linear variations, although with a poorer fit for a specific WTW. This indicates that global functions could be used for initial modelling of these, and similar WTW, without the need for costly WTW specific model calibration data.

- Correlation between predicted and observed free chlorine concentrations using the adopted two stage approach at each of the six WTWs was found satisfactory, although the relationship weakened with time. The average difference between observed and predicted chlorine concentrations across the six WTWs decreased from 0.039 mg/l (2.9 %) after five minutes, to 0.047 mg/l (4.1 %) after one-hour, and 0.061 mg/l (6.7 %) after two-hours.

% increase in R^2 values	**0-5 (60 mins)**	**30.72**
	5-10 (60 mins)	**1.65**
	10-15 (60 mins)	**0.21**
	0-5 (120 mins)	**25.80**
	5-10 (120 mins)	**2.44**
	10-15 (120 mins)	**1.09**

Table 5.1; Percentage increases in the R^2 values with the removal of greater lengths of the initial time period of tests.

	Coefficients for equations of the form; $X = A + (a \cdot C_0) + (b \cdot \Theta) + (c \cdot TOC) + (d \cdot Br)$				
L.H.S of equation	**Constant**	**Initial Cl (C_0)**	**Temp. (Θ)**	**TOC**	**Br**
X	**A**	**a**	**b**	**c**	**d**
WHITACRE					
Kb ~ 5-30 mins	0.1945	-0.2230	0.0107	0.1277	-0.0017
Kb ~ 5-60 mins	0.1949	-0.2411	0.0113	0.1023	-0.0009
Kb ~ 5-90 mins	0.1304	-0.1829	0.0095	0.0883	-0.0014
Kb ~ 5-120 mins	0.0989	-0.1610	0.0086	0.0837	-0.0015
Initial 5 mins factor	0.9404	0.0299	-0.0034	-0.0598	0.0016
MELBOURNE					
Kb ~ 5-30 mins	0.5297	-0.3781	0.0047	0.1166	0.0064
Kb ~ 5-60 mins	0.2426	-0.2443	0.0083	0.0272	0.0042
Kb ~ 5-90 mins	0.2140	-0.2075	0.0072	0.0188	0.0033

Kb ~ 5-120 mins	0.1518	-0.1624	0.0069	0.0191	0.0026
Initial 5 mins factor	1.0219	0.0046	-0.0037	0.0143	-0.0041
DRAYCOTE					
Kb ~ 5-30 mins	0.0698	-0.1875	0.0147	0.0901	?
Kb ~ 5-60 mins	0.2129	-0.2105	0.0087	0.0697	?
Kb ~ 5-90 mins	0.2005	-0.1644	0.0051	0.0572	?
Kb ~ 5-120 mins	0.1475	-0.1329	0.0056	0.0467	?
Initial 5 mins factor	1.0224	0.0266	-0.0043	-0.0606	?
CAMP. HILLS					
Kb ~ 5-30 mins	0.3833	-0.3333	0.0141	-0.0349	0.0054
Kb ~ 5-60 mins	0.2769	-0.2419	0.0090	-0.0283	0.0042
Kb ~ 5-90 mins	0.1804	-0.1721	0.0073	-0.0171	0.0032
Kb ~ 5-120 mins	0.0901	-0.1084	0.0063	0.00006	0.0021
Initial 5 mins factor	0.9345	0.0484	-0.0051	-0.0480	0.0007
CHURCH WILNE					
Kb ~ 5-30 mins	0.1663	-0.1915	0.0103	0.1536	?
Kb ~ 5-60 mins	0.1071	-0.1090	0.0053	0.1141	?
Kb ~ 5-90 mins	0.0989	-0.1096	0.0055	0.1004	?
Kb ~ 5-120 mins	0.0085	-0.0892	0.0041	0.0854	?
Initial 5 mins factor	0.9235	0.0304	-0.0027	-0.0738	?
STRENSHAM					

Kb ~ 5-30 mins	0.6743	-0.4982	0.0119	0.1251	-0.0004
Kb ~ 5-60 mins	0.2904	-0.2551	0.0089	0.0952	-0.0003
Kb ~ 5-90 mins	0.1477	-0.1718	0.0082	0.0811	-0.00002
Kb ~ 5-120 mins	0.1274	-0.1495	0.0071	0.0677	0.00013
Initial 5 mins factor	0.7945	0.1108	-0.0029	-0.0538	0.00007

Table 5.2; Coefficients to be used in equation 5.3 at each of the six WTWs (question marks indicate the omission of bromide in the calculated equations due to insufficient / erroneous bromide data.

Sample site (WTW) / Location		**Temp. (^{o}C) range**	**TOC (mg/l) range**	**C_0 (mg/l) range**	**Bulk decay over 8 hours**		
					k_b (l/hr) range	**R^2 value range**	**Mean**
Whitacre	**F.W**	**17.1 – 17.4**	**2.76 – 2.94**	**0.50 – 0.53**	**0.048 - 0.064**	**0.84 – 0.9**	**0.056**
	D.S	**17.1 – 17.4**	**2.57 – 2.75**	**0.14 – 0.26**	**0.034 – 0.048**	**0.80 – 0.98**	**0.041**
Melbourne	**F.W**	**14.9 – 16.7**	**2.69 – 3.0**	**0.43 – 0.47**	**0.047 – 0.051**	**0.95 – 0.98**	**0.049**
	D.S	**15.5**	**1.57**	**0.18**	**0.041**	**0.92**	**0.041**
Draycote	**F.W**	**17.8 – 22.1**	**3.63 – 4.82**	**0.42 – 0.50**	**0.047 – 0.068**	**0.88 – 0.95**	**0.062**
	D.S	**17.8 –**	**3.63 –**	**0.15 –**	**0.026 –**	**0.84 –**	**0.028**

		18.6	**3.83**	**0.16**	**0.029**	**0.95**	
Campion Hills	**F.W**	**18.0 – 18.6**	**2.59 – 3.06**	**0.42 – 0.48**	**0.035 – 0.044**	**0.73 – 0.93**	**0.039**
	D.S	**18.0 – 18.5**	**2.7 – 3.13**	**0.23 – 0.37**	**0.025 – 0.030**	**0.89 – 0.97**	**0.0275**
Church Wilne	**F.W**	**15.5 – 19.5**	**1.7 – 1.71**	**0.51 – 0.57**	**0.039 – 0.068**	**0.77 – 0.85**	**0.051**
	D.S	**15.4**	**1.57**	**0.18**	**0.041**	**0.92**	**0.041**
Strensham	**F.W**	**4.1 – 21.5**	**1.33 – 2.91**	**0.32 – 0.52**	**0.037 – 0.093**	**0.86 – 0.99**	**0.062**
	D.S (1)	**4.1 – 20.8**	**1.35 – 2.83**	**0.21 – 0.37**	**0.023 – 0.067**	**0.86 – 0.98**	**0.046**
	D.S (2)	**4.1 – 17.2**	**1.35 – 2.95**	**0.11 – 0.23**	**0.016 – 0.042**	**0.81 – 0.98**	**0.028**

Table 5.3; Summary of bulk decay tests at each of the six WTW final waters and sampling point in distribution systems, over 8 hours**.**

Sample site (WTW) / Location		**Temp. (^{o}C) range**	**TOC (mg/l) range**	**C_0 (mg/l) range**	**Bulk decay over 24 hours**		
					k_b (l/hr) range	**R^2 value range**	**Mean**
Whitacre	**F.W**	**17.1 – 17.4**	**2.76 – 2.94**	**0.5 – 0.53**	**0.03 – 0.033**	**0.88 – 0.92**	**0.032**
	D.S	**17.1 – 17.4**	**2.57 – 2.75**	**0.14 – 0.26**	**0.02 – 0.038**	**0.89 – 0.98**	**0.029**
Melbourne	**F.W**	**14.9 – 16.7**	**2.69 - 3**	**0.43 – 0.47**	**0.031 – 0.046**	**0.98 – 0.99**	**0.039**
	D.S	**15.5**	**1.57**	**0.18**	**0.035**	**0.92**	**0.035**
Draycote	**F.W**	**17.8 – 22.1**	**3.63 – 4.82**	**0.42 – 0.50**	**0.027 – 0.039**	**0.92 – 0.96**	**0.034**

	D.S	**17.8 – 18.6**	**3.63 – 3.83**	**0.15 – 0.16**	**0.023 – 0.025**	**0.98 – 0.98**	**0.024**
Campion Hills	**F.W**	**18.0 – 18.6**	**2.59 – 3.06**	**0.42 – 0.48**	**0.025 – 0.027**	**0.93 – 0.98**	**0.026**
	D.S	**18.0 – 18.5**	**2.7 – 3.13**	**0.23 – 0.37**	**0.017 – 0.018**	**0.91 – 0.96**	**0.018**
Church Wilne	**F.W**	**15.5 – 19.5**	**1.7 – 1.71**	**0.51 – 0.57**	**0.037 – 0.040**	**0.92 – 0.96**	**0.0385**
	D.S	**15.4**	**1.57**	**0.18**	**0.035**	**0.98**	**0.035**
Strensham	**F.W**	**4.1 – 21.5**	**1.33 – 2.91**	**0.32 – 0.52**	**0.022 – 0.054**	**0.9 – 0.99**	**0.041**
	D.S (1)	**4.1 – 20.8**	**1.35 – 2.83**	**0.21 – 0.37**	**0.016 – 0.041**	**0.9 – 0.98**	**0.031**
	D.S (2)	**4.1 – 17.2**	**1.35 – 2.95**	**0.11 – 0.23**	**0.013 – 0.036**	**0.94 – 0.99**	**0.023**

Table 5.4; Summary of bulk decay tests at each of the six WTW final waters and sampling point in distribution systems, over 24 hours.

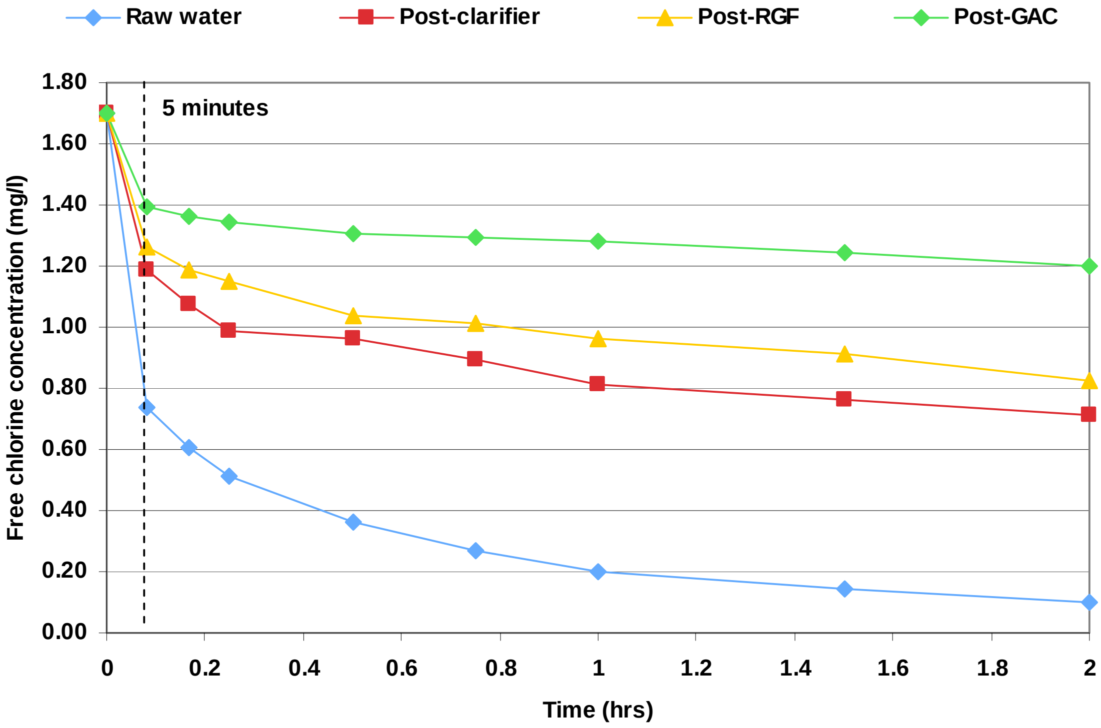


Figure 5.1; Profile of free chlorine concentrations over two-hour bulk decay tests on raw, post-clarifier, post-RGF and post-GAC waters from Strensham WTW on the 26.02.08 sampling day.

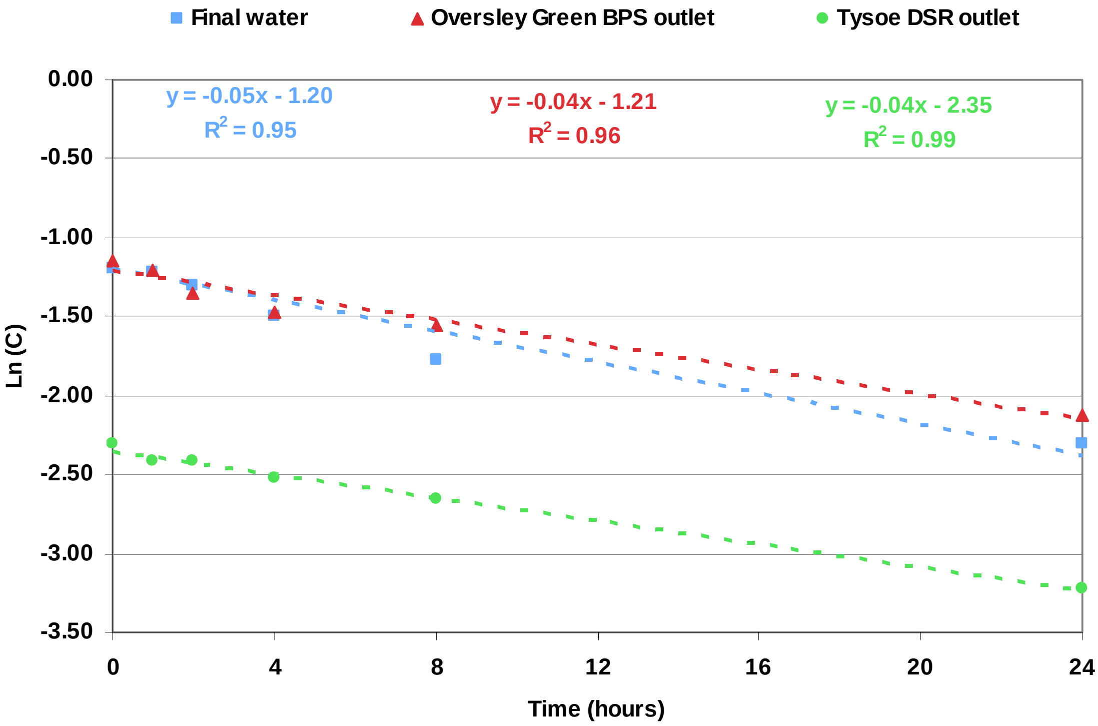


Figure 5.2; Examples of the fitting of first order relationships to chlorine decay at Strensham WTW final water and two locations in the Shipston distribution system.

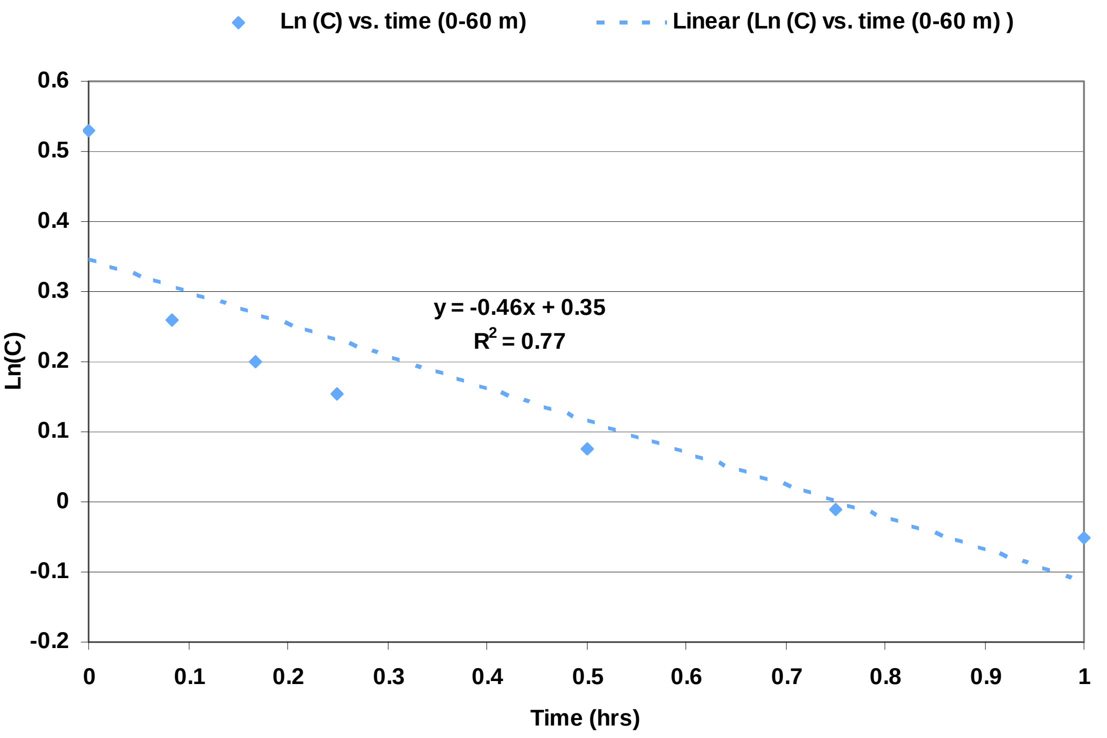


Figure 5.3; Example of determination of 1st order bulk decay constants over a one hour time period. Test conducted on post-GAC water at a C_0 of 1.7 mg/l.

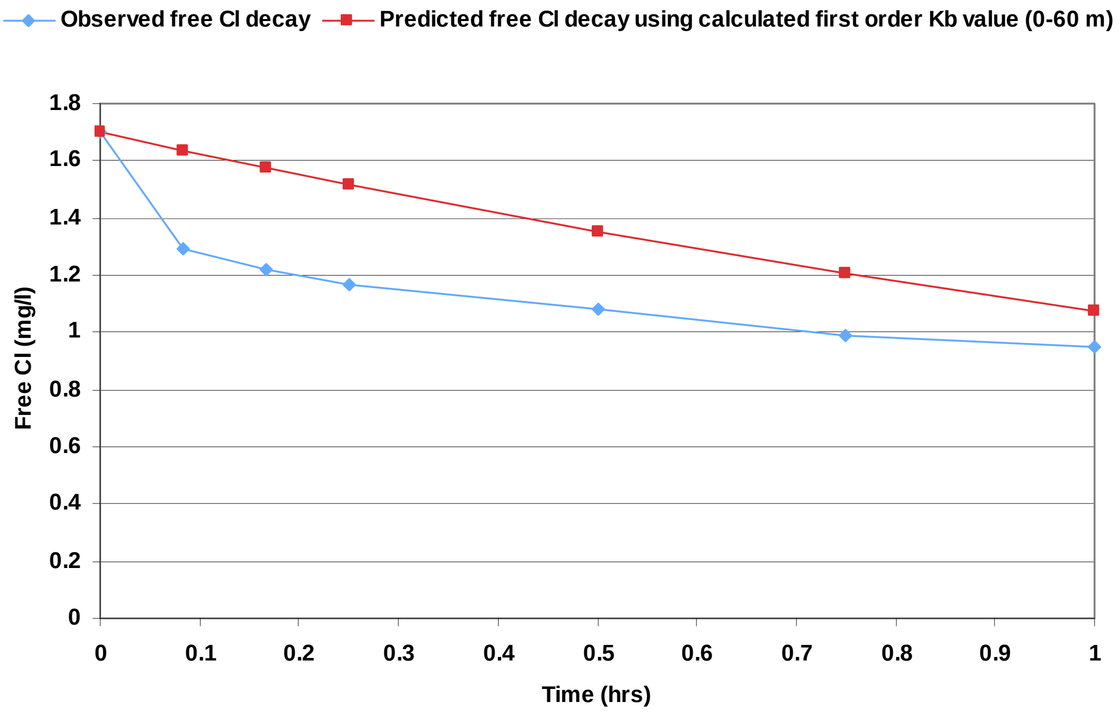


Figure 5.4; Example of observed vs. predicted (using 1st order bulk decay constant from Figure 5.3) free chlorine concentrations over 1 hour.

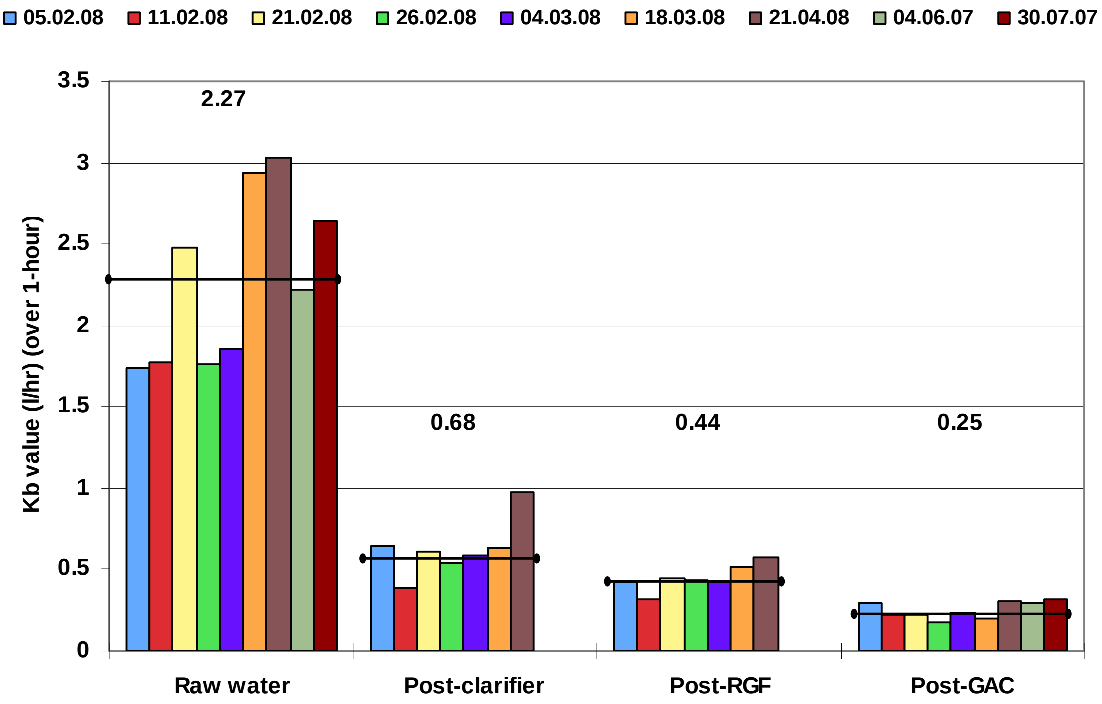


Figure 5.5; Bulk decay constants at the raw, post-clarifier, post-RGF and post-GAC sampling points at Strensham WTW. All tests over 1-hour at a temperature of 15°C and initial free chlorine concentration of 1.7 mg/l.

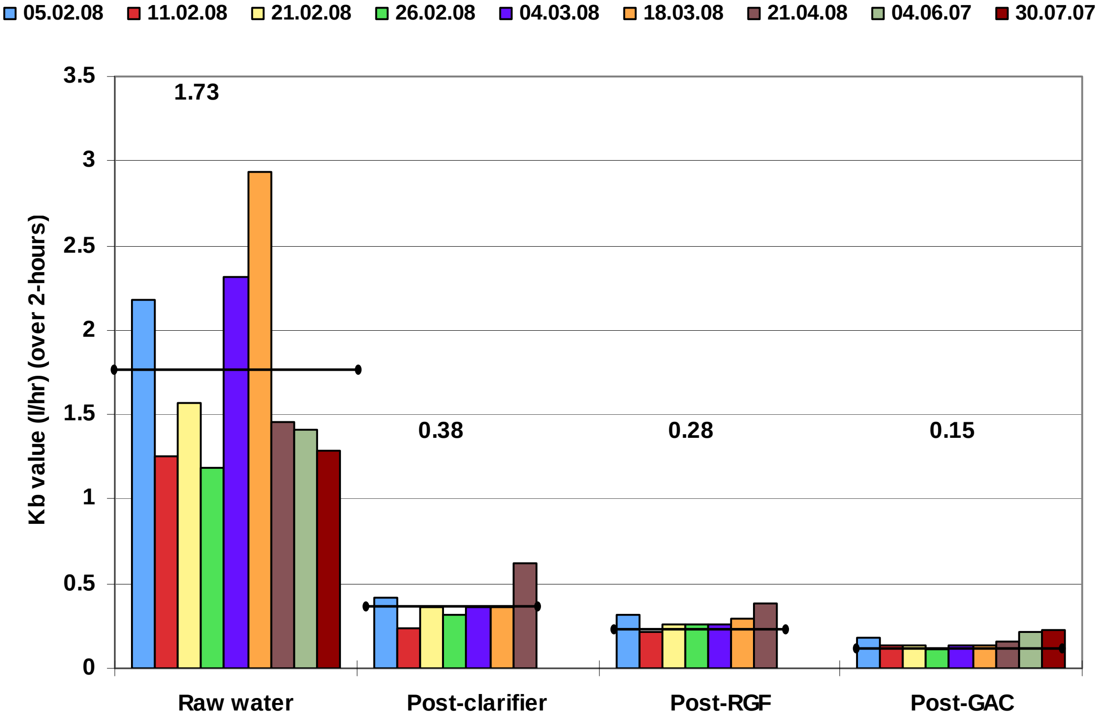


Figure 5.6; Bulk decay constants at the raw, post-clarifier, post-RGF and post-GAC sampling points at Strensham WTW. All tests over 2-hours at a temperature of 15°C and initial free chlorine concentration of 1.7 mg/l.

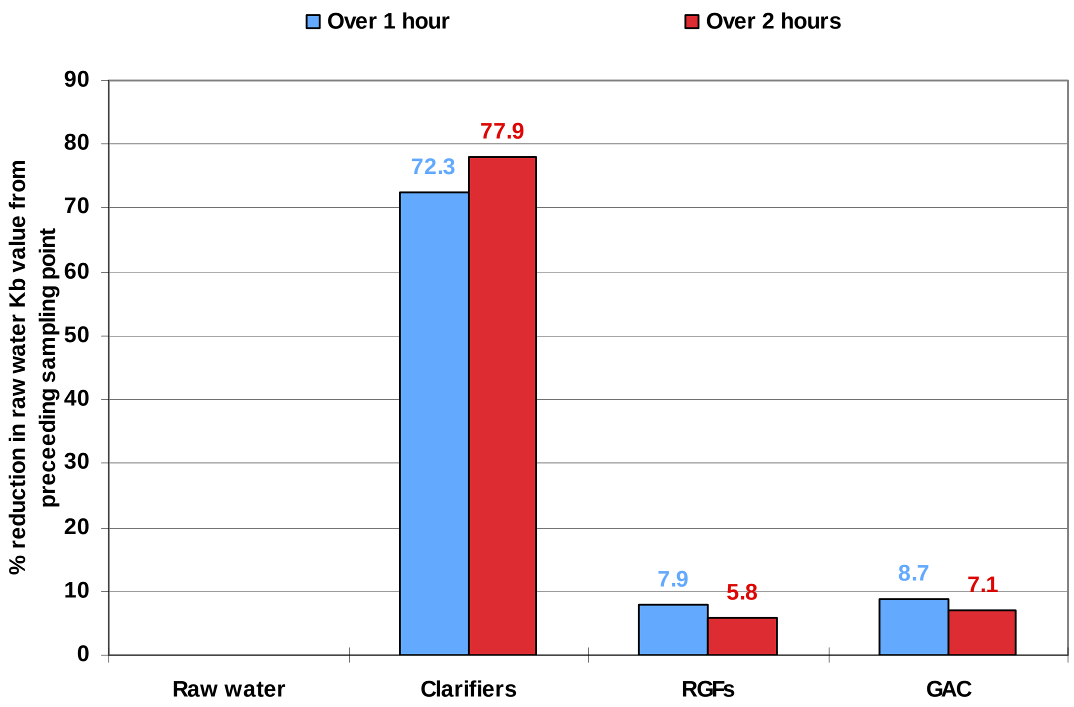


Figure 5.7; Percentage reductions in mean bulk decay constants from raw water sampling point, over 1 hour and 2 hour tests through Strensham WTW.

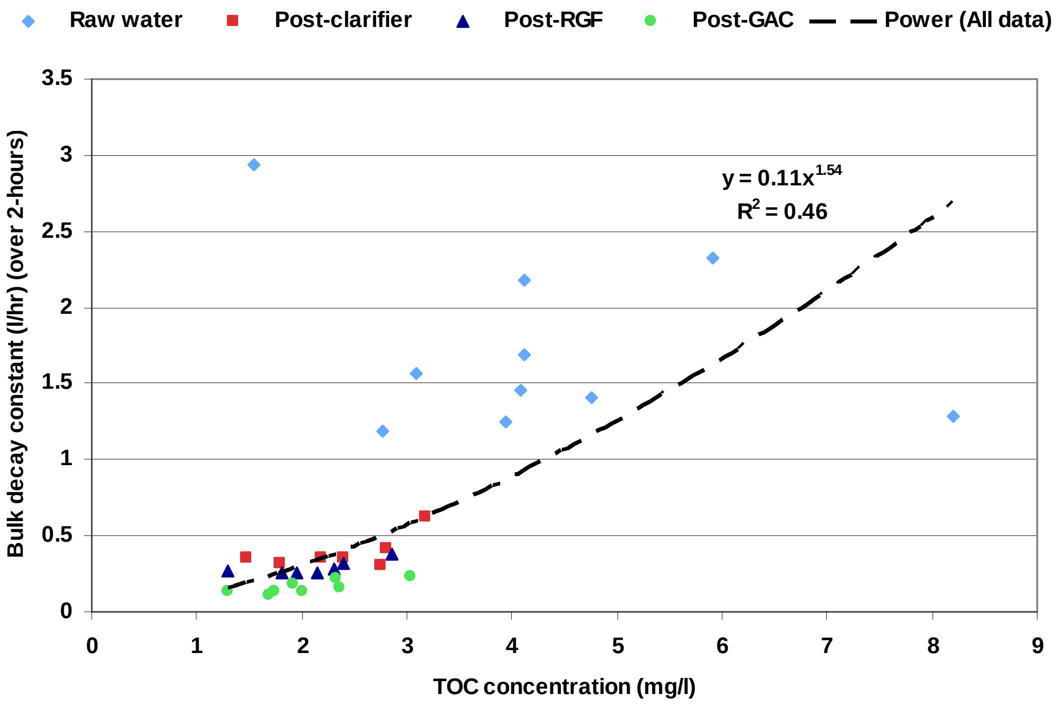


Figure 5.8; TOC concentrations vs. bulk decay constants over 2-hours for all bulk decay tests at Strensham WTW. All tests conducted at an initial chlorine concentration of 1.7 mg/l and a temperature of 15 ^{o}C.

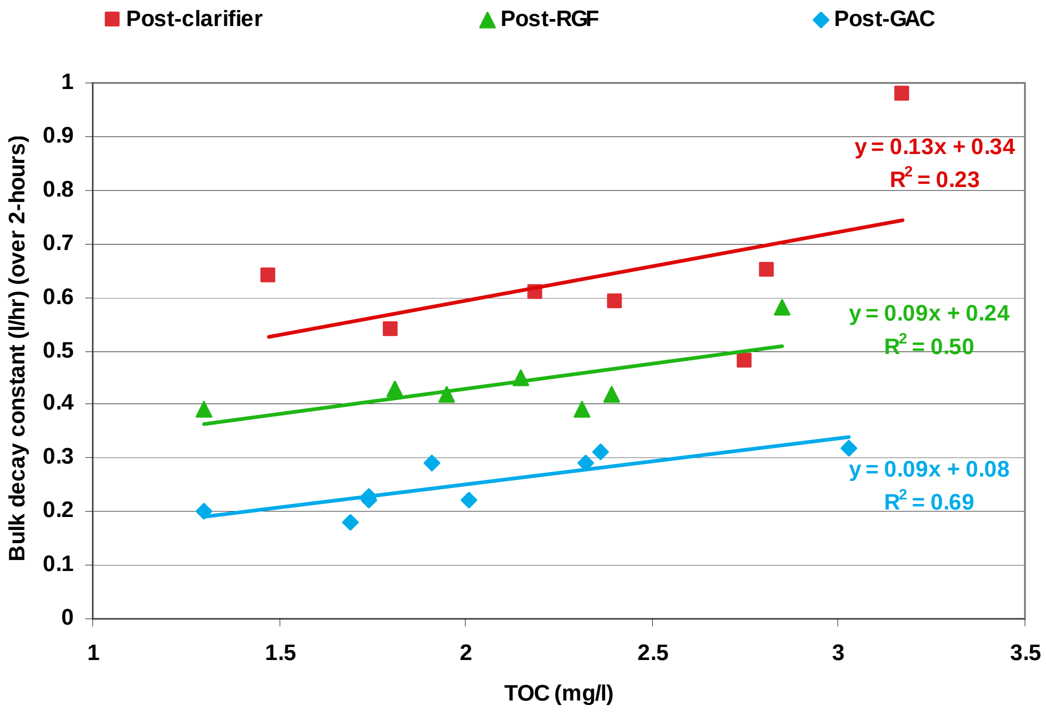


Figure 5.9; Bulk decay constants (over 2 hours) vs. TOC concentrations from samples taken through Strensham WTW. All tests over 2-hours at a temperature of 15°C and initial free chlorine concentration of 1.7 mg/l.

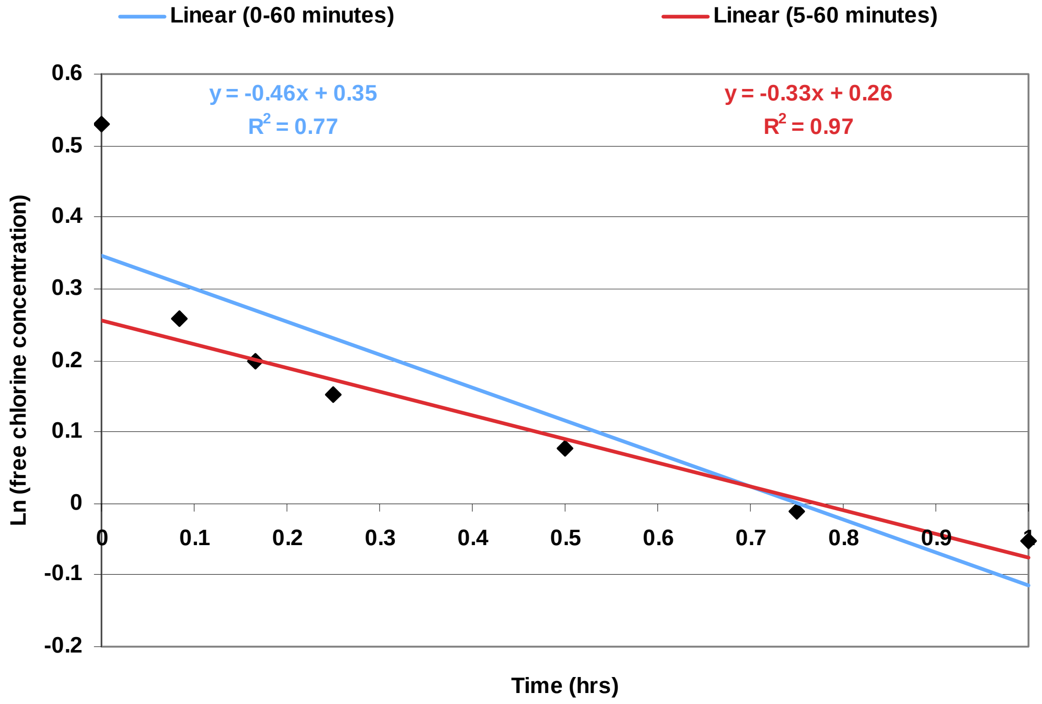


Figure 5.10; Example of the improvement in 1st order fit to chlorine decay with the omission of the initial five-minutes of the test period.

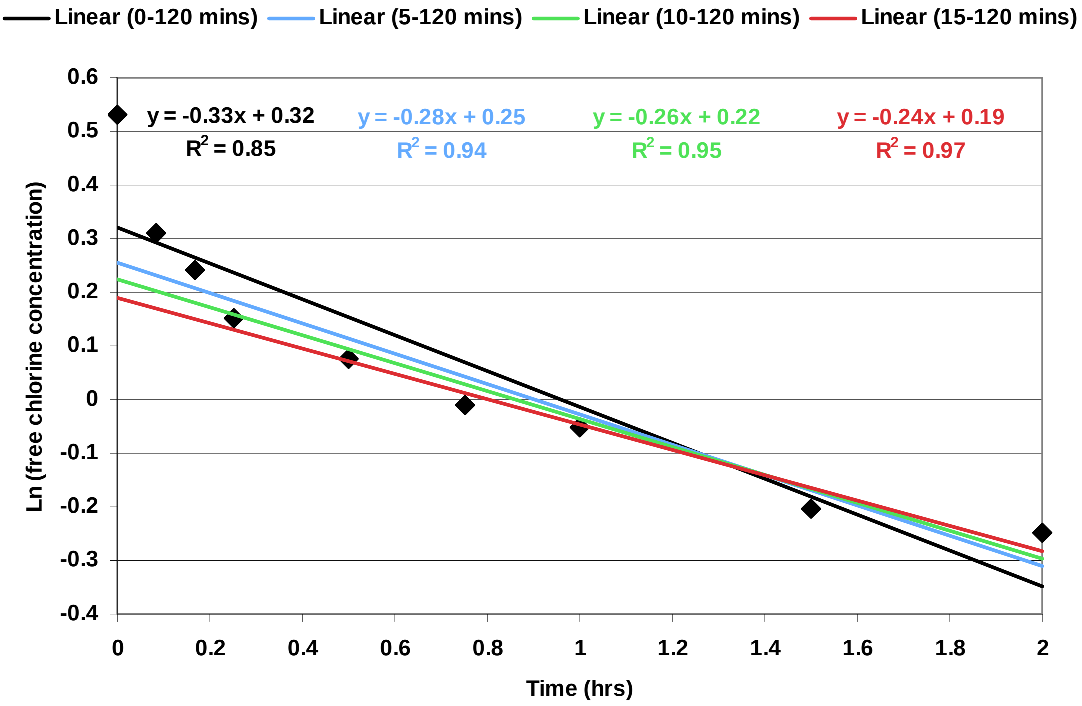


Figure 5.11; Example of the change in accuracy of first order relationship with the different time periods used for ln(C) vs. time.

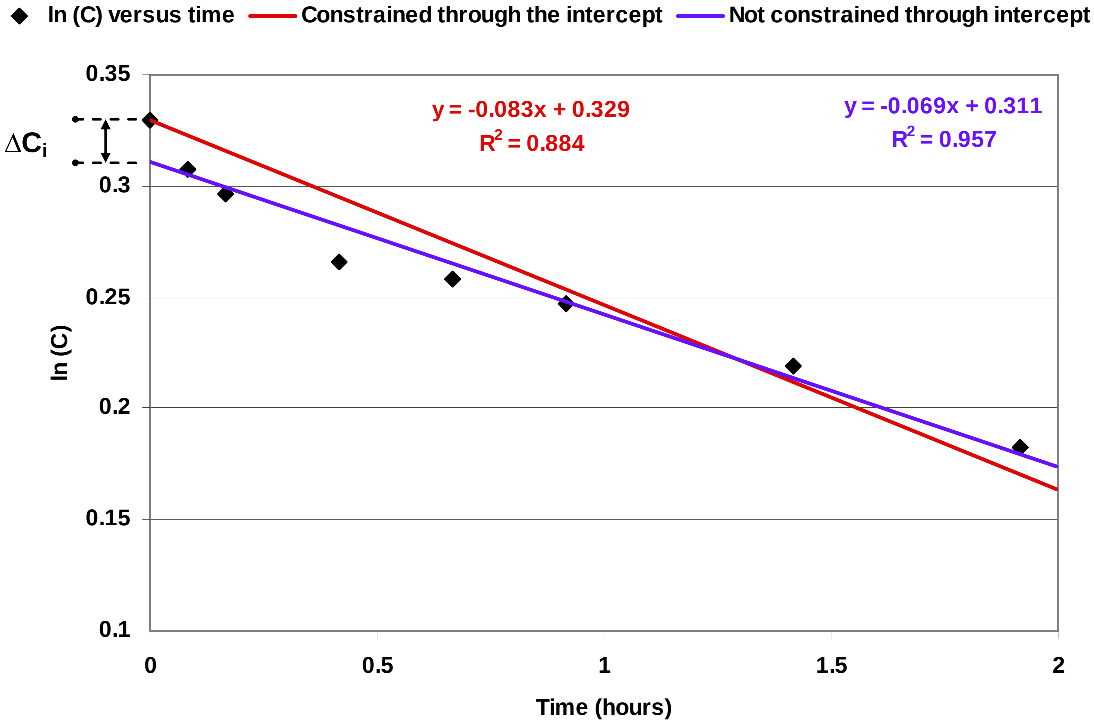


Figure 5.12; Example of the improvement in 1st order fit to chlorine decay with the best fit line unconstrained (blue) compared to constrained (red) through C_{5mins}.

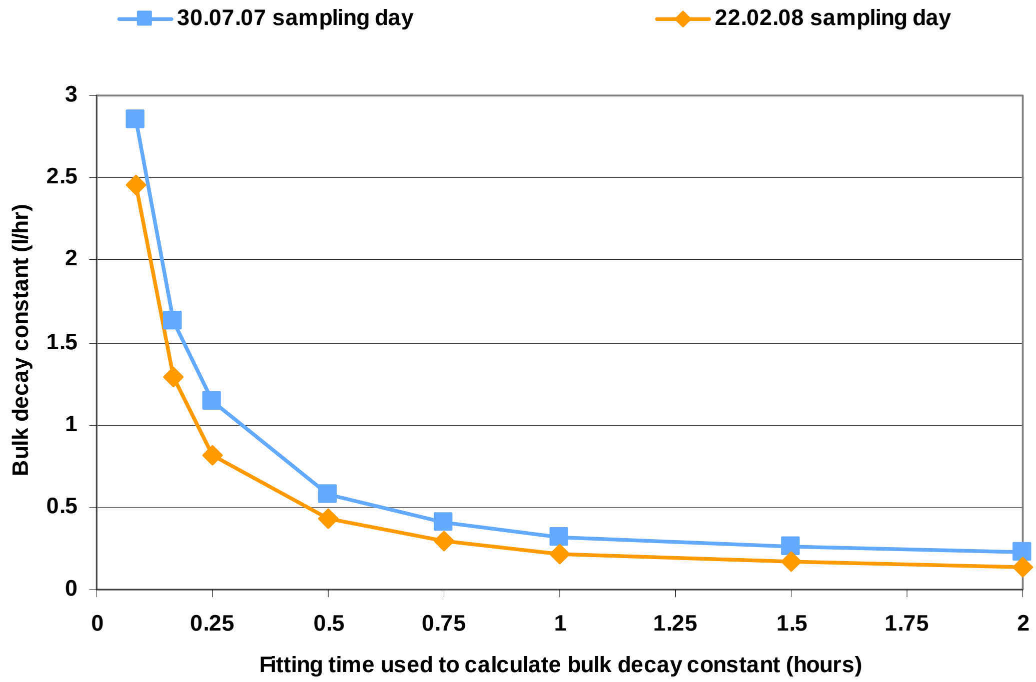


Figure 5.13; Two examples of the change in bulk decay constants with the time used to calculate them. Both tests conducted at 15 °C at an initial chlorine concentration of 1.7 mg/l.

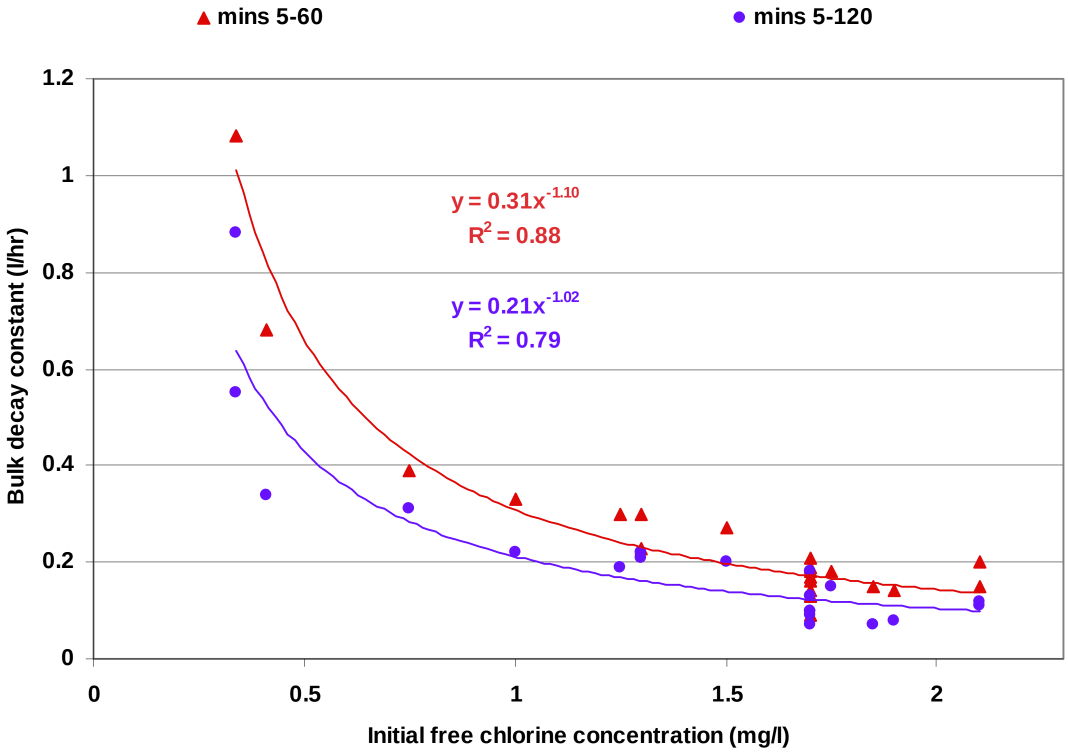


Figure 5.14; Relationship between bulk decay constants and C_0 for all tests on Strensham post-GAC water (over 5-60 and 5-120 minutes).

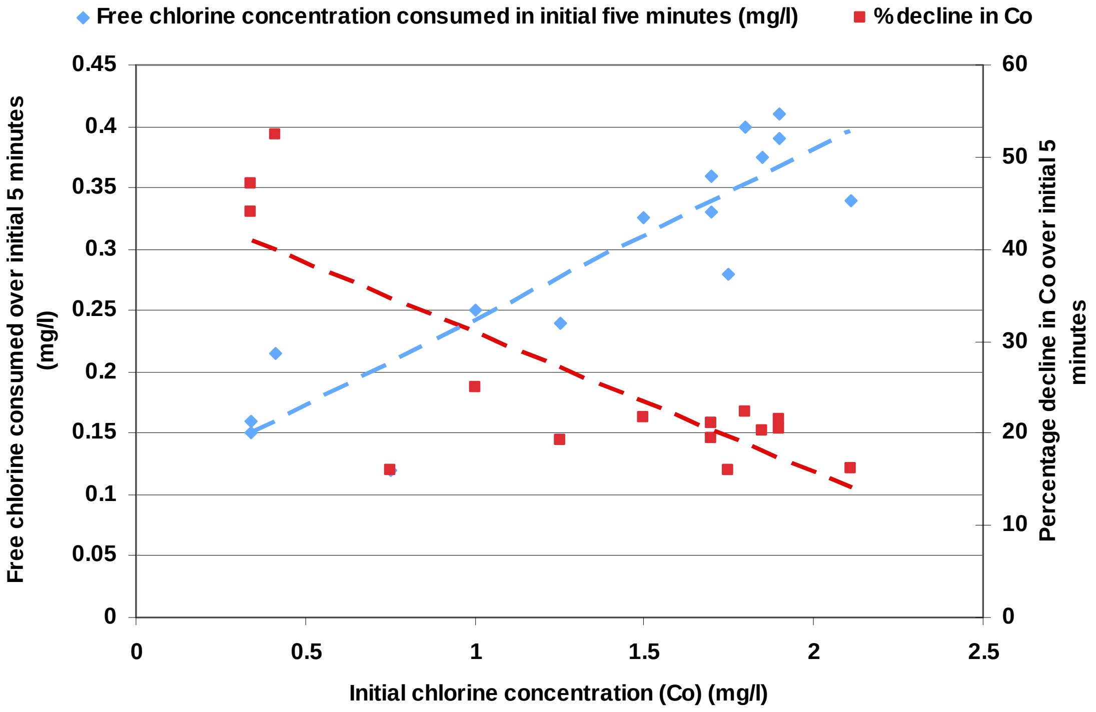


Figure 5.15; Relationship between C_0 and the percentage decline and free chlorine consumed in the initial five-minutes of all tests on Strensham post-GAC water.

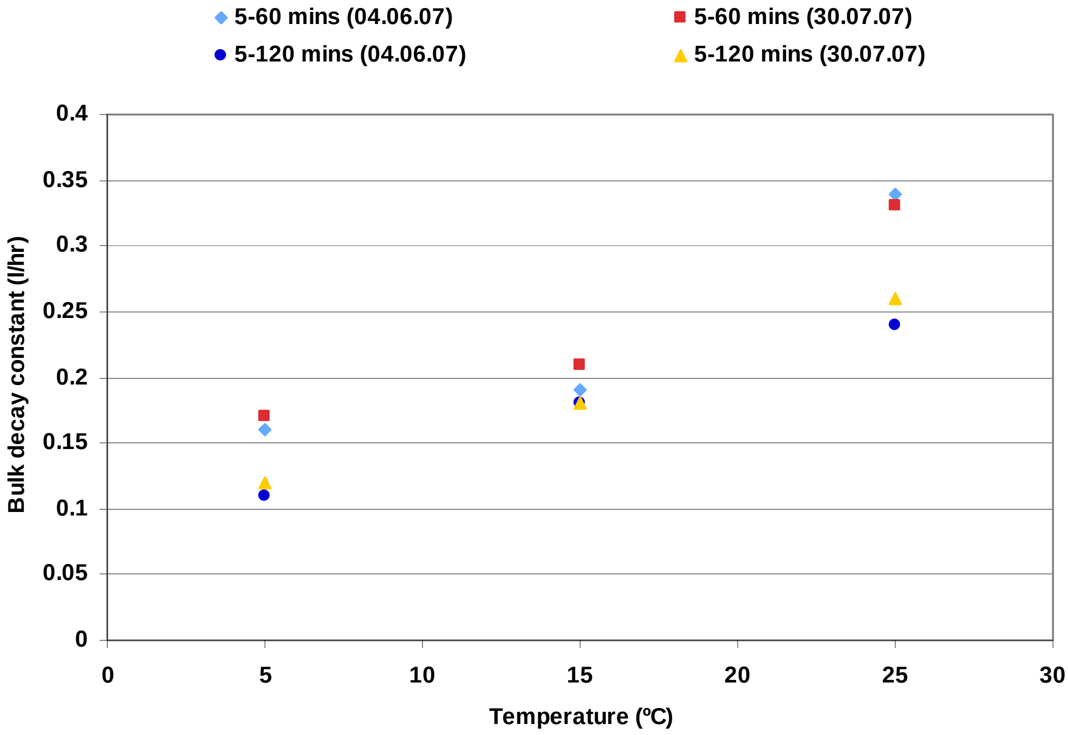


Figure 5.16; Relationship between bulk decay constants and temperature for tests on Strensham post-GAC water on two summer 2007 sampling days.

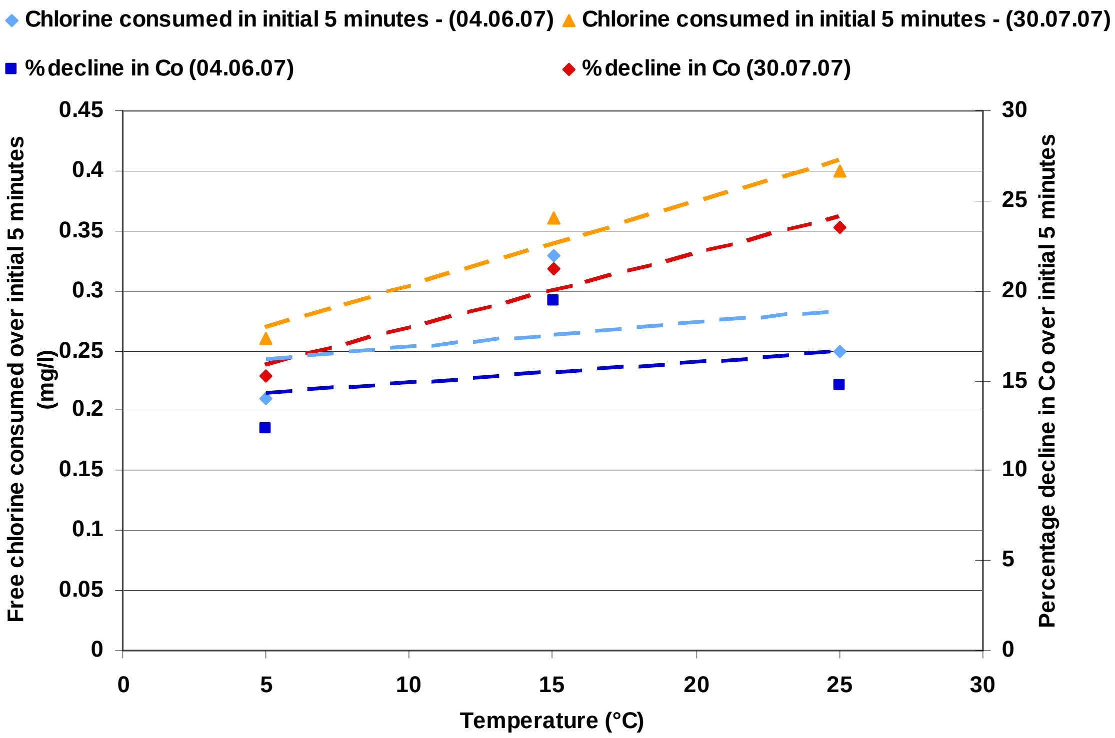


Figure 5.17; Relationship between temperature and the percentage decline and free chlorine consumed in the initial five-minutes of tests on Strensham post-GAC water on two summer 2007 sampling days.

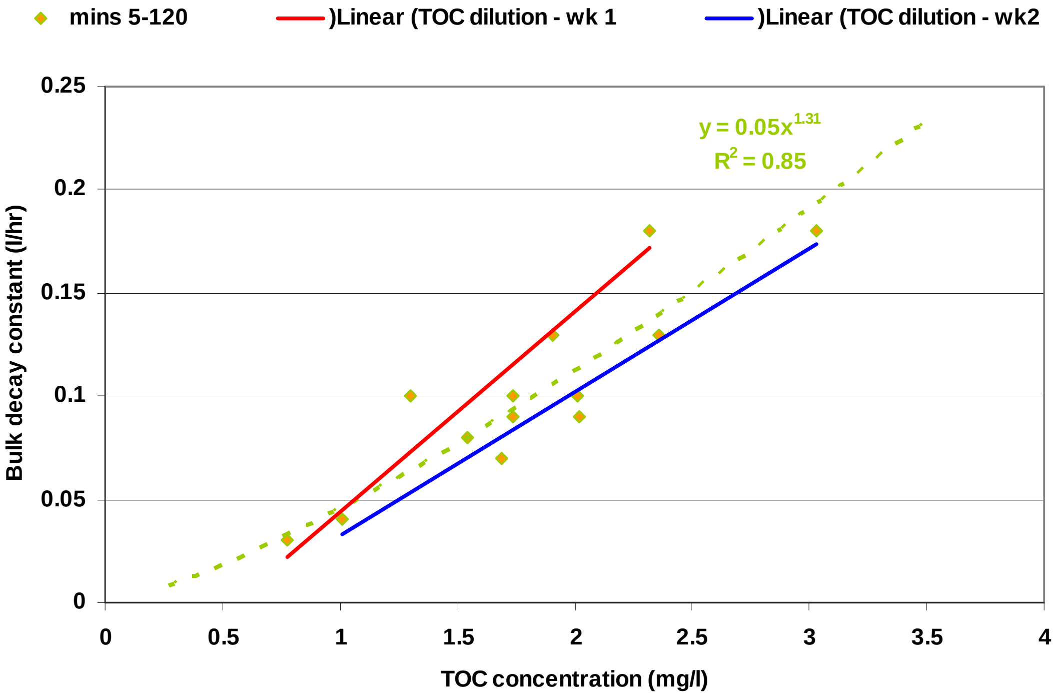


Figure 5.18; TOC concentrations vs. bulk decay constants for all tests on Strensham post-GAC water at 15 ^{o}C and an initial chlorine concentration of 1.7 mg/l. Sample water dilution tests shown with separate linear trend lines.

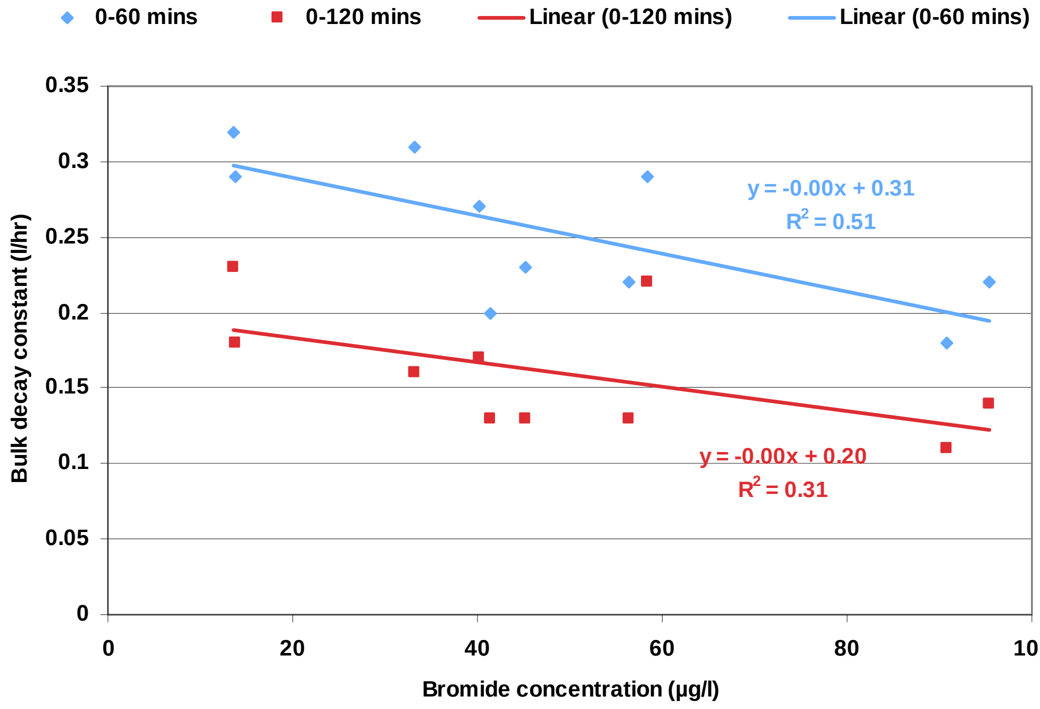


Figure 5.19; Post-GAC bromide concentrations vs. bulk decay constants over 0-60 and 0-120 minute periods for all tests conducted at an initial chlorine concentration of 1.7 mg/l and temperature of 15°C at Strensham WTW.

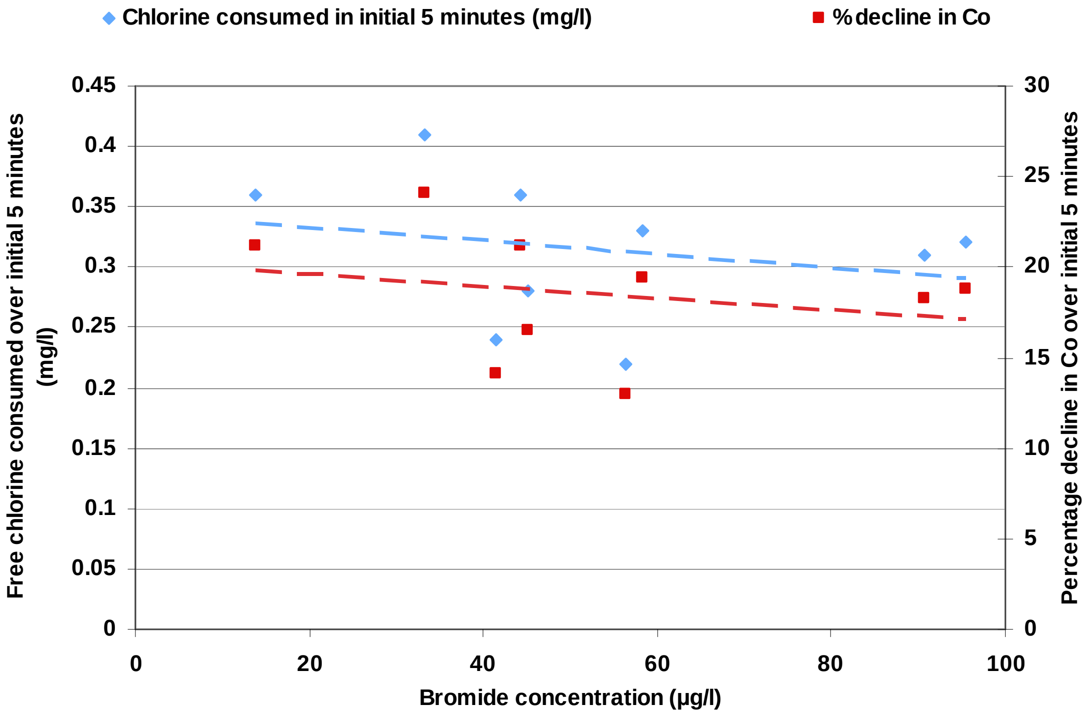


Figure 5.20; Relationship between bromide concentrations and the percentage decline and free chlorine consumed in the initial five-minutes of tests on Strensham post-GAC water.

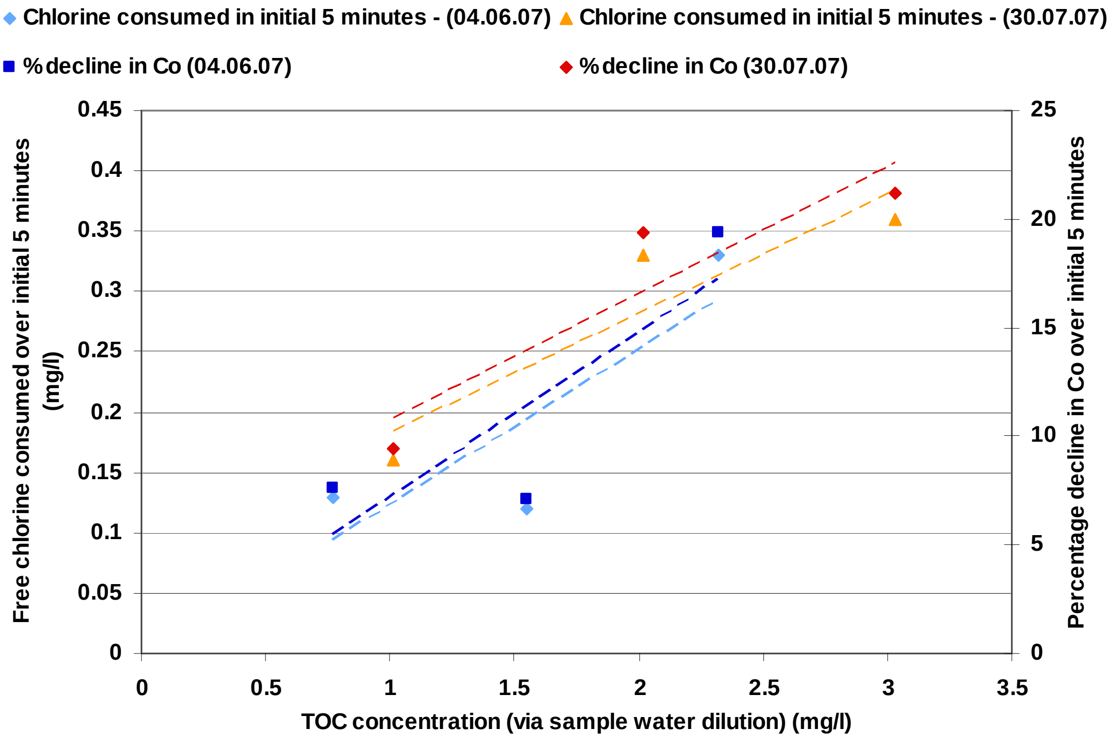


Figure 5.21; Relationship between TOC concentration (via sample water dilution) and the percentage decline and free chlorine consumed in the initial five-minutes of tests on Strensham post-GAC water on two summer 2007 sampling days.

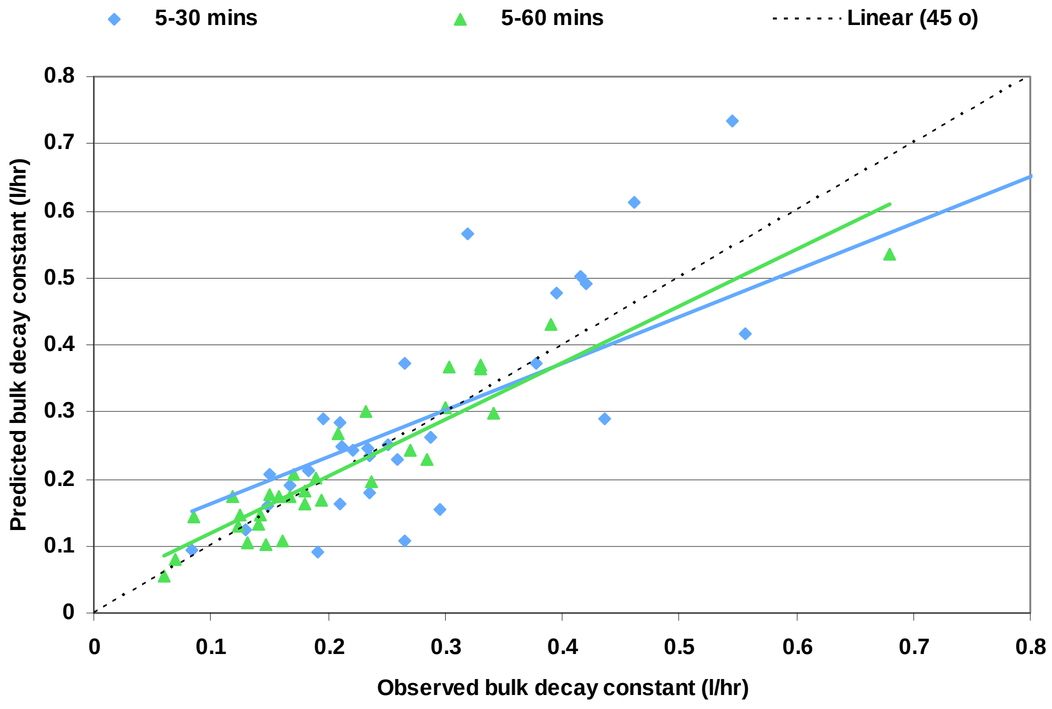


Figure 5.22; Observed bulk decay constants versus predicted bulk decay constants (calculated via stepwise regression) between 5-30 minutes and 5-60 minutes. 45^o line (dotted black line).

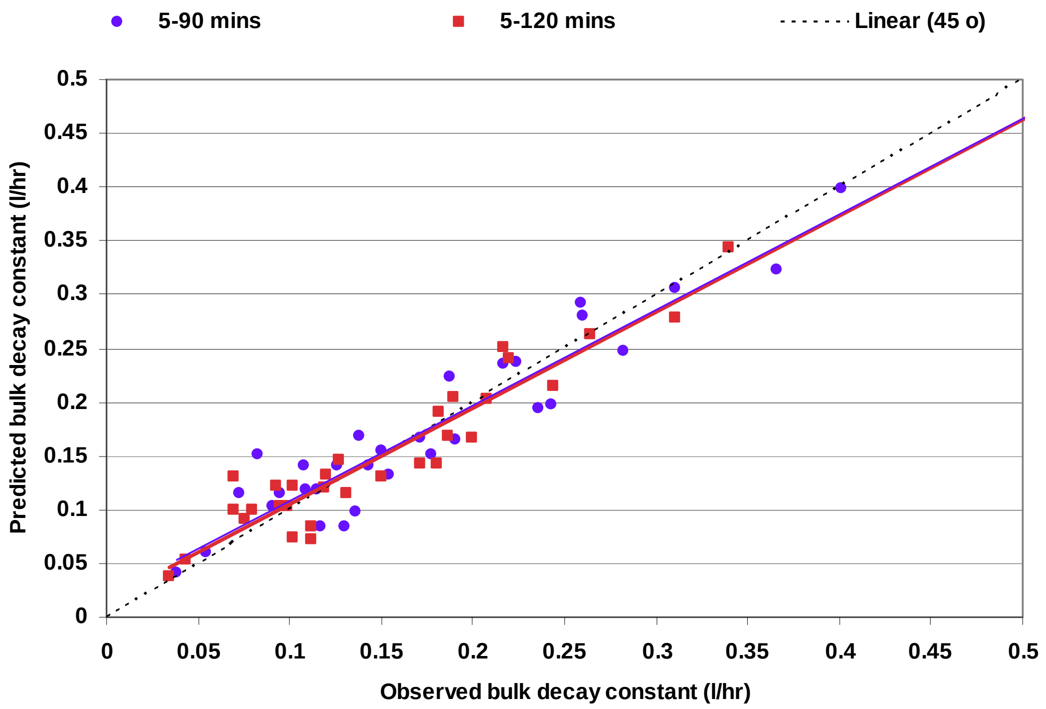


Figure 5.23; Observed bulk decay constants versus predicted bulk decay constants (calculated via stepwise regression) between 5-90 minutes and 5-120 minutes. 45^{o} line (dotted black line).

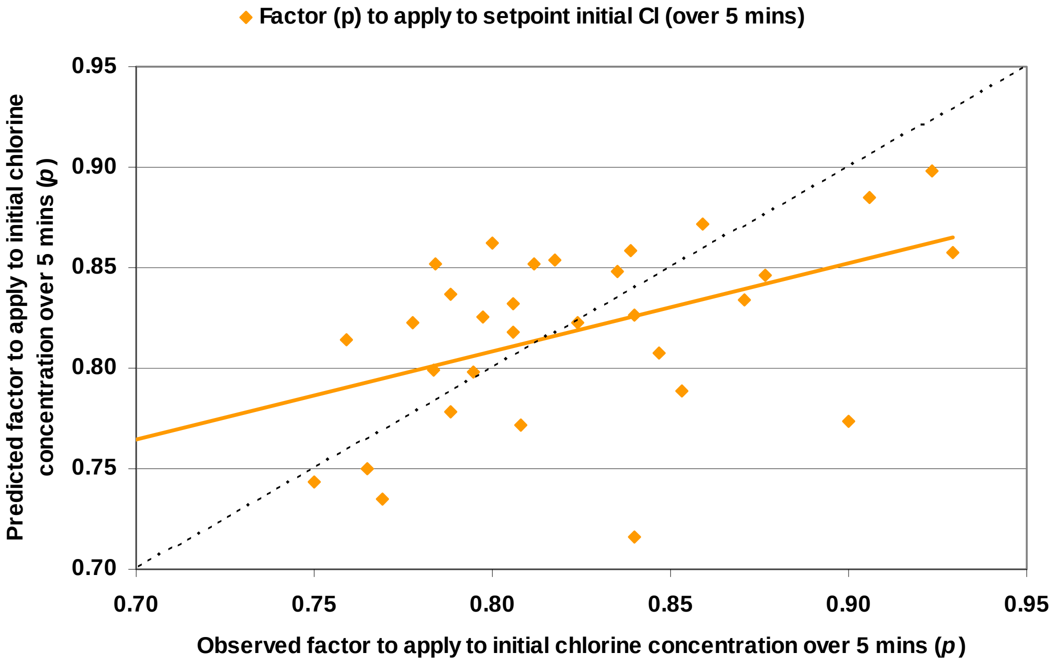


Figure 5.24; Observed vs. predicted factors to apply to initial chlorine concentration to represent drop in free chlorine concentration (calculated via stepwise regression). 45^{o} line (dotted black line).

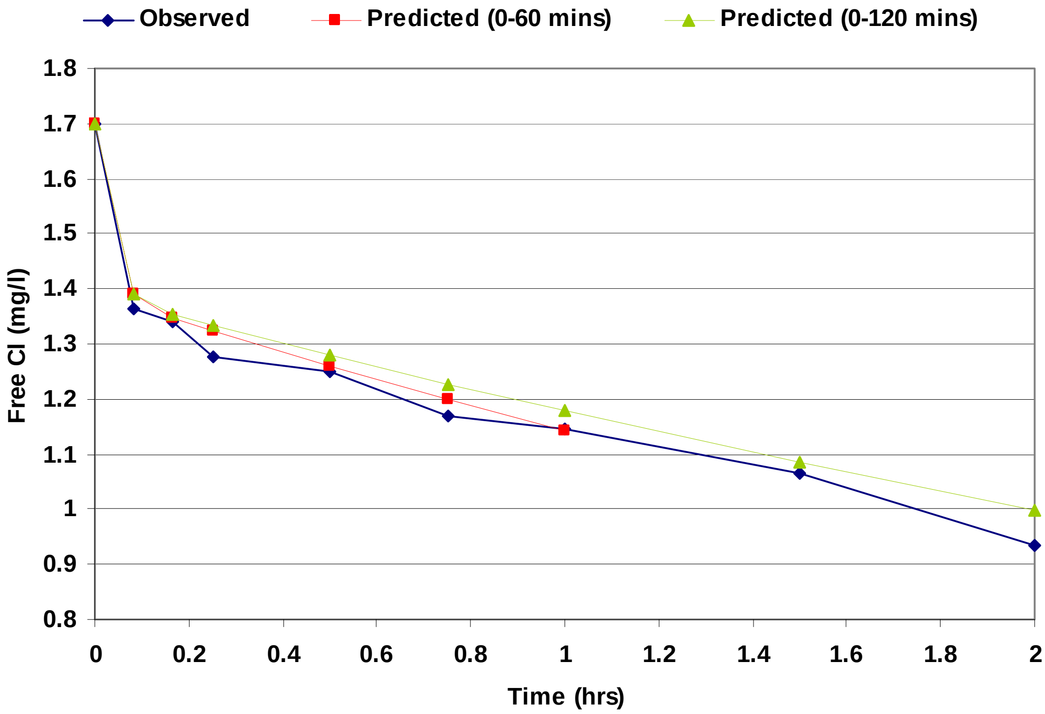


Figure 5.25; Example of the application of the two stage modelling approach using SPSS derived equations for determining free chlorine concentrations with time.

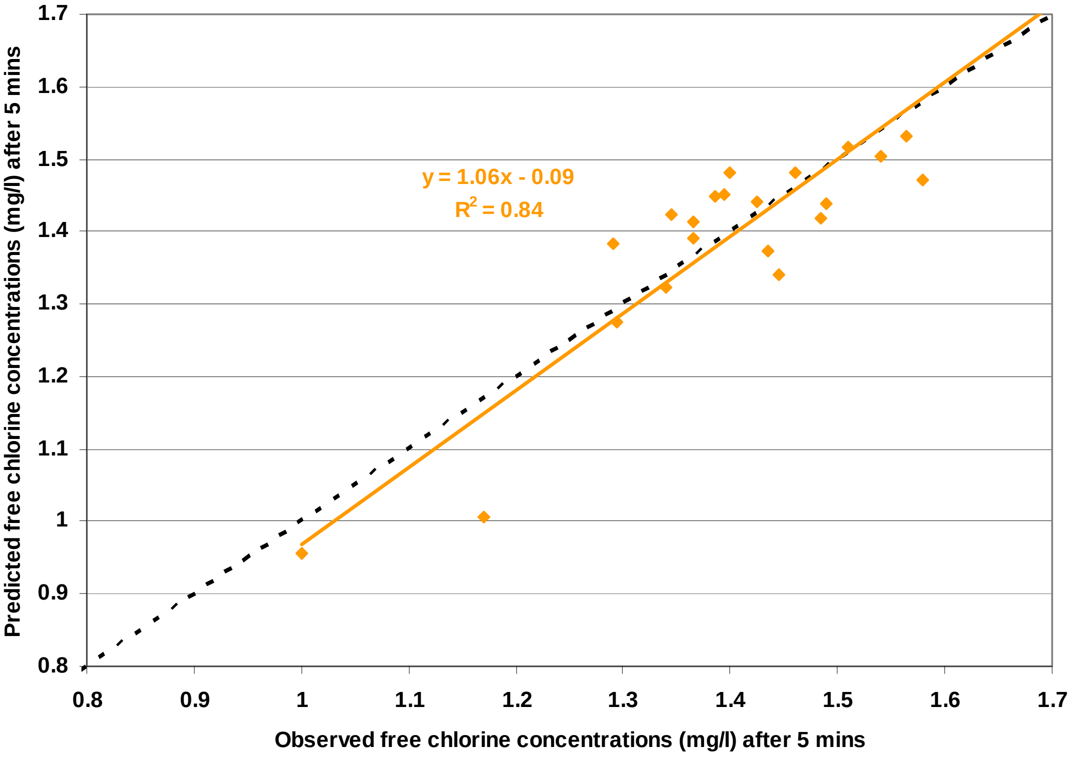


Figure 5.26; Observed versus predicted free chlorine concentrations after 5 minutes using predictive equations

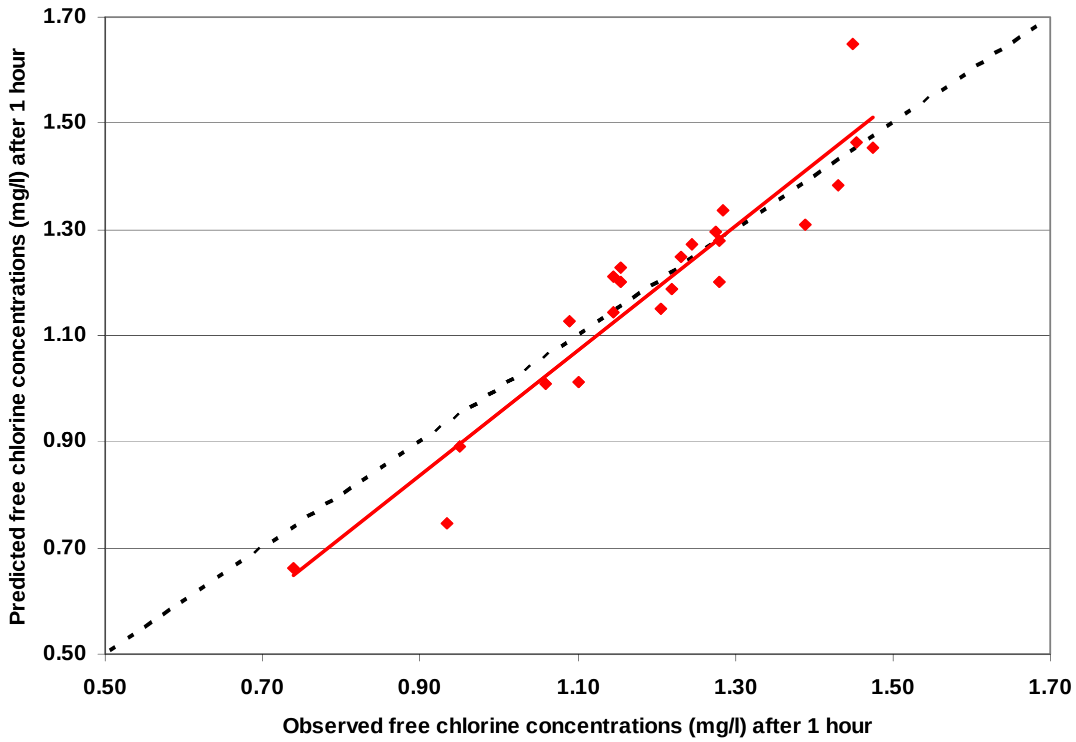


Figure 5.27; Observed versus predicted free chlorine concentrations after 1-hour using predictive equations.

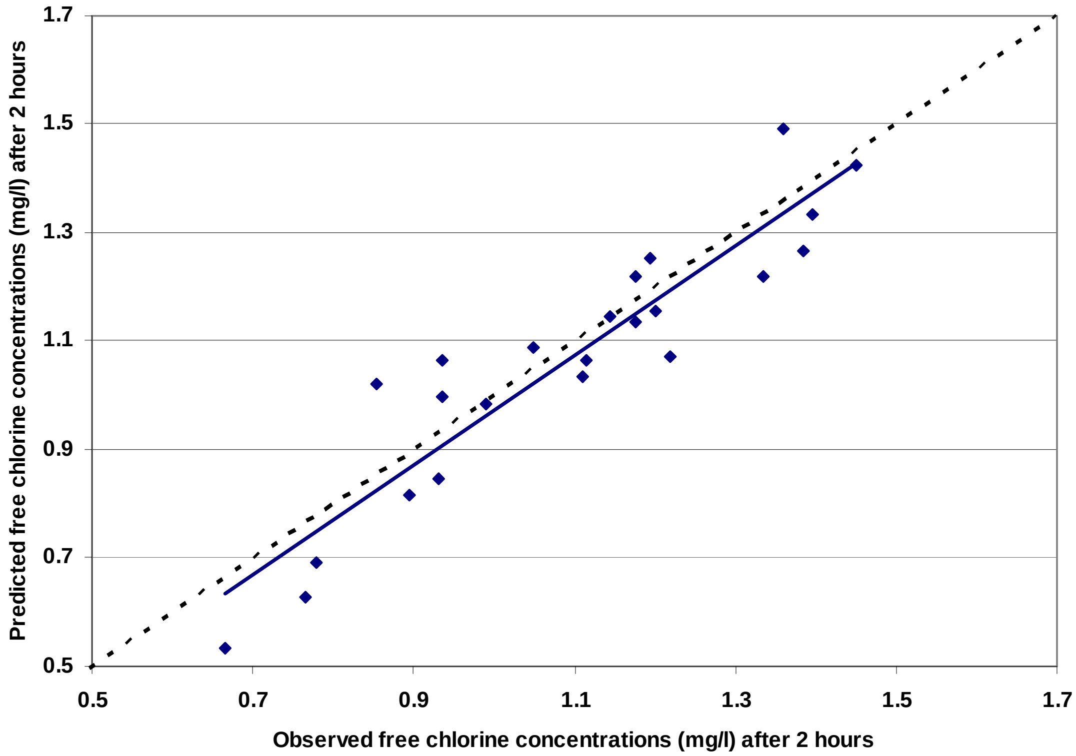


Figure 5.28; Observed versus predicted free chlorine concentrations after 2-hours using predictive equations.

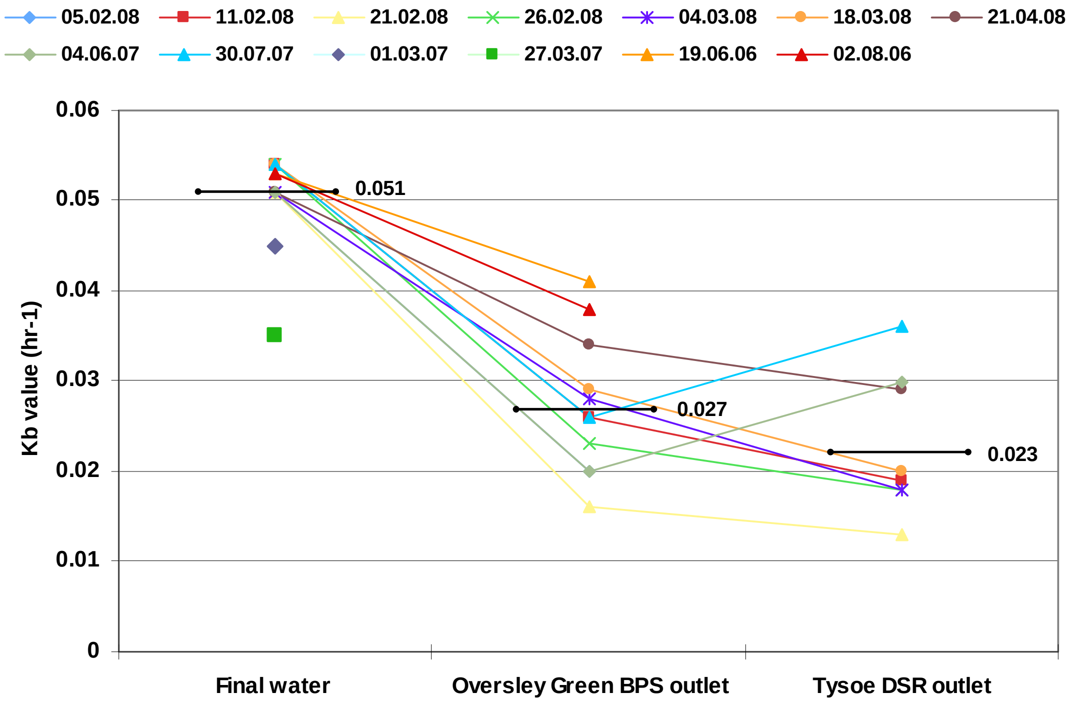


Figure 5.29; Bulk decay constants (over 24 hours) from tests on Strensham Final, Oversley Green BPS outlet and Tysoe DSR outlet waters. All tests conducted over 24 hours at the ambient initial chlorine concentration and temperature.

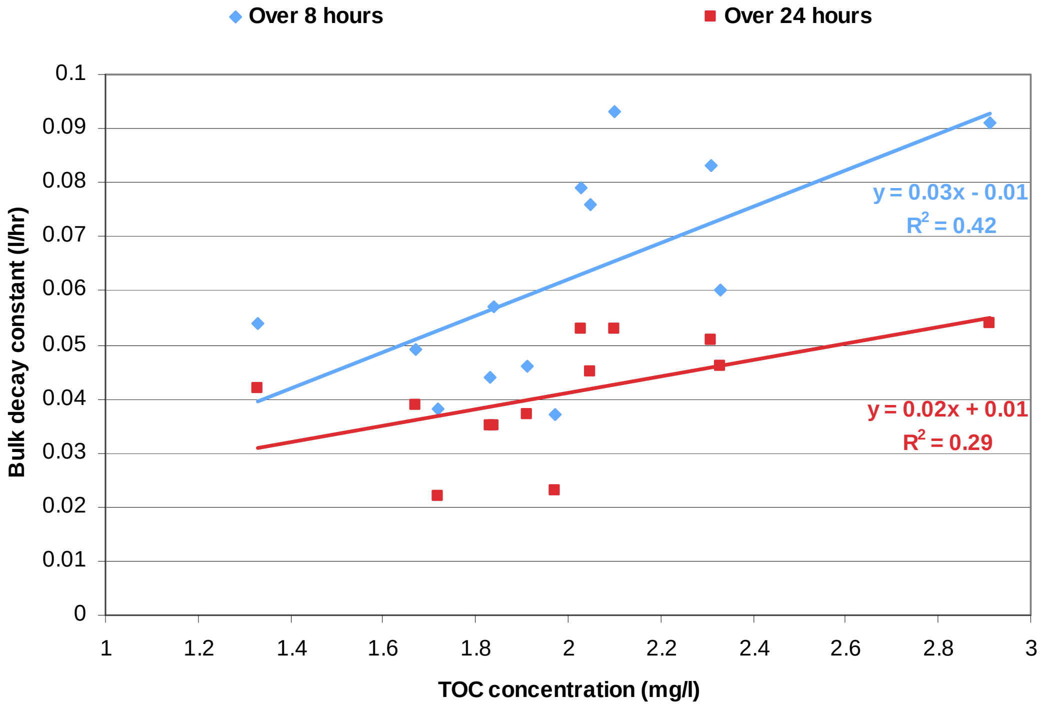


Figure 5.30; TOC concentrations vs. bulk decay constants over 8 and 24 hours at Strensham WTW final water on different sampling days at ambient temperature and chlorine concentrations.

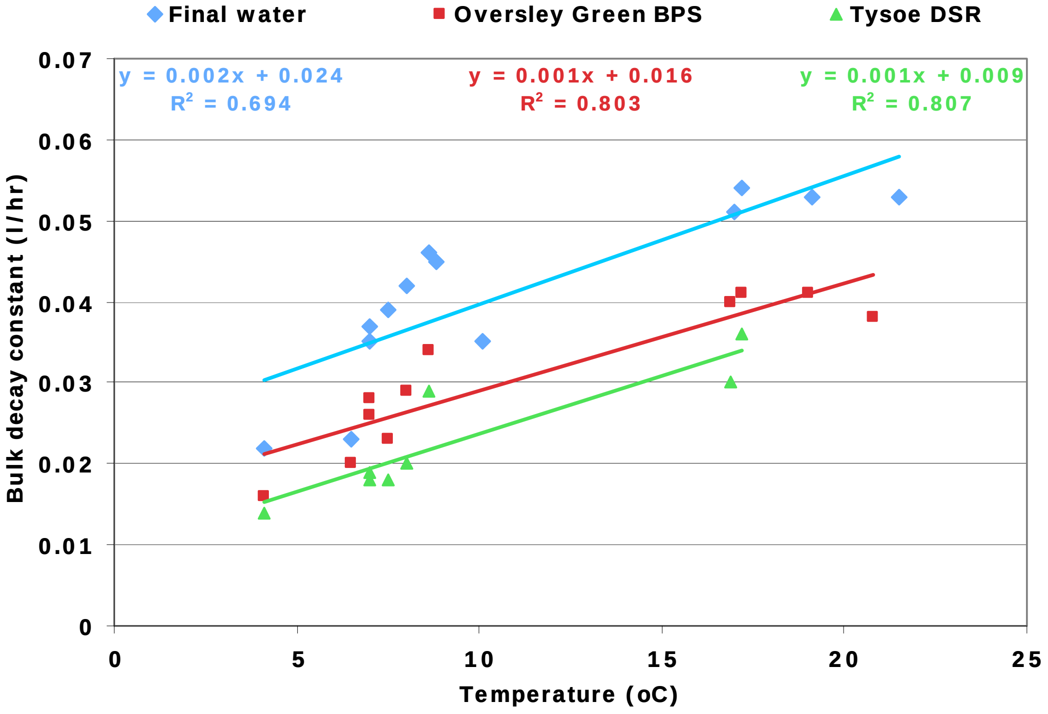


Figure 5.31; Bulk decay constants over 24-hours (at ambient initial chlorine concentrations) vs. temperature at Strensham WTW final water, Oversley Green BPS outlet and Tysoe DSR outlet.

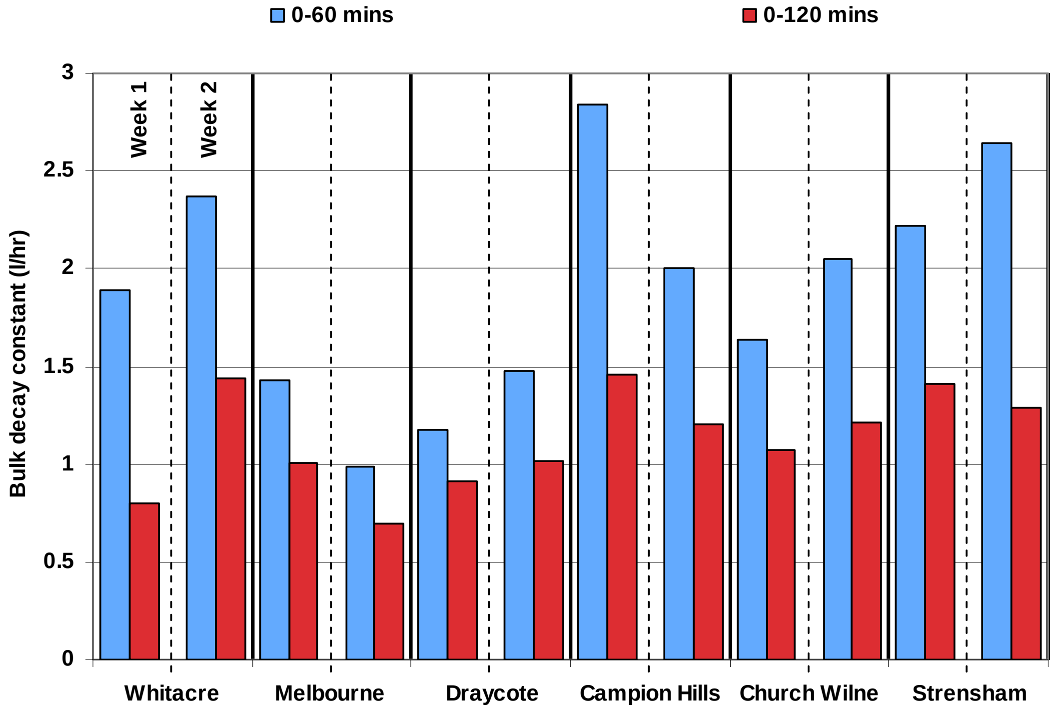


Figure 5.32; Summary of bulk decay constants over 1 and 2 hours on tests on six WTWs raw waters. Each test conducted at 15°C and an initial chlorine concentration of 1.7 mg/l.

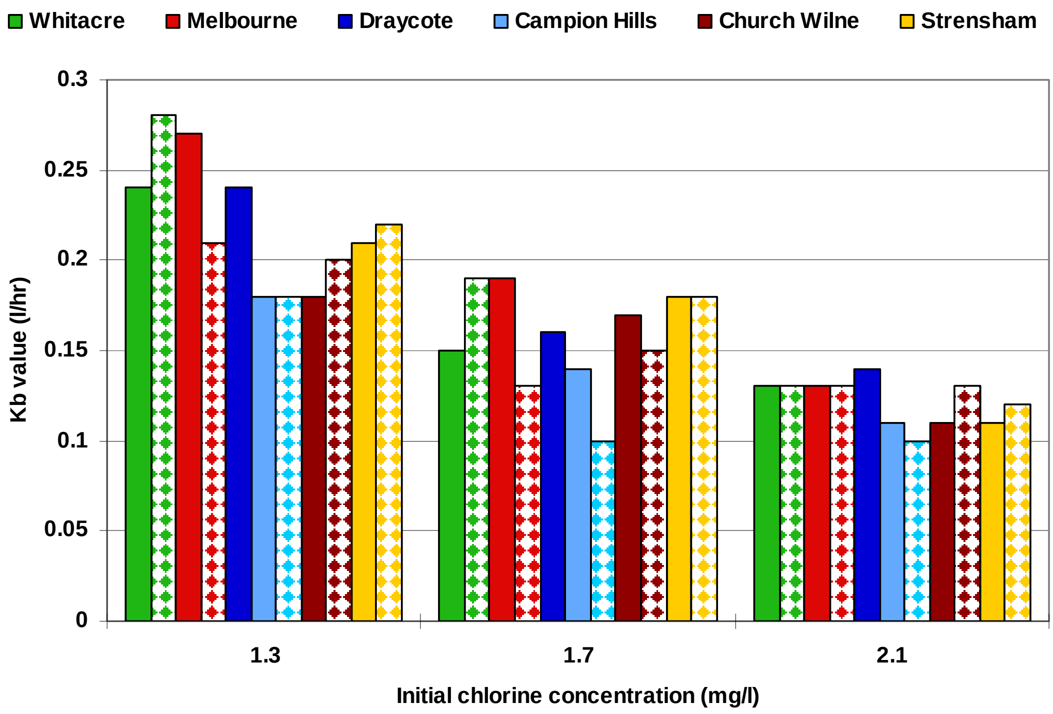


Figure 5.33; Bulk decay constants (between 5-120 mins) with the variation in initial chlorine concentration at each of the six WTWs. All tests conducted at ambient pH and TOC concentration, at a temperature of 15 °C. Chequered bars for 2nd sampling week.

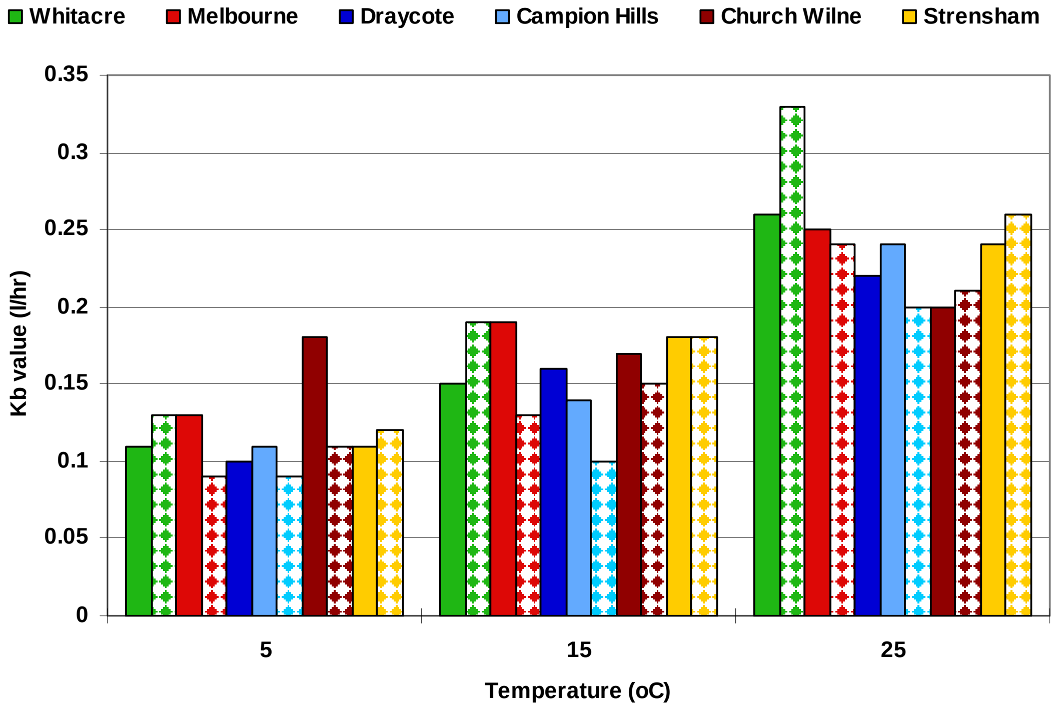


Figure 5.34; Bulk decay constants (between 5-120 mins) with the variation in temperature at each of the six WTWs. All tests conducted at ambient pH and TOC concentration, with an initial chlorine concentration of 1.7 mg/l. Chequered bars for 2nd sampling week.

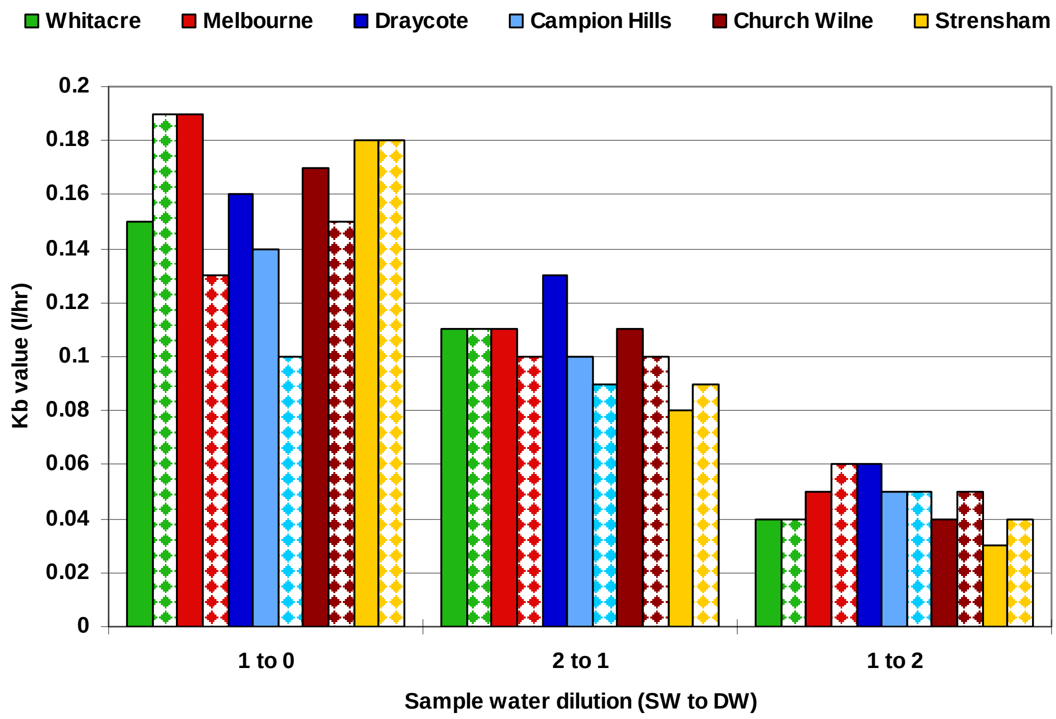


Figure 5.35; Bulk decay constants (between 5-120 mins) with the variation in sample water dilution at each of the six WTWs. All tests conducted at ambient pH, an initial chlorine concentration of 1.7 mg/l and a temperature of 15 °C.

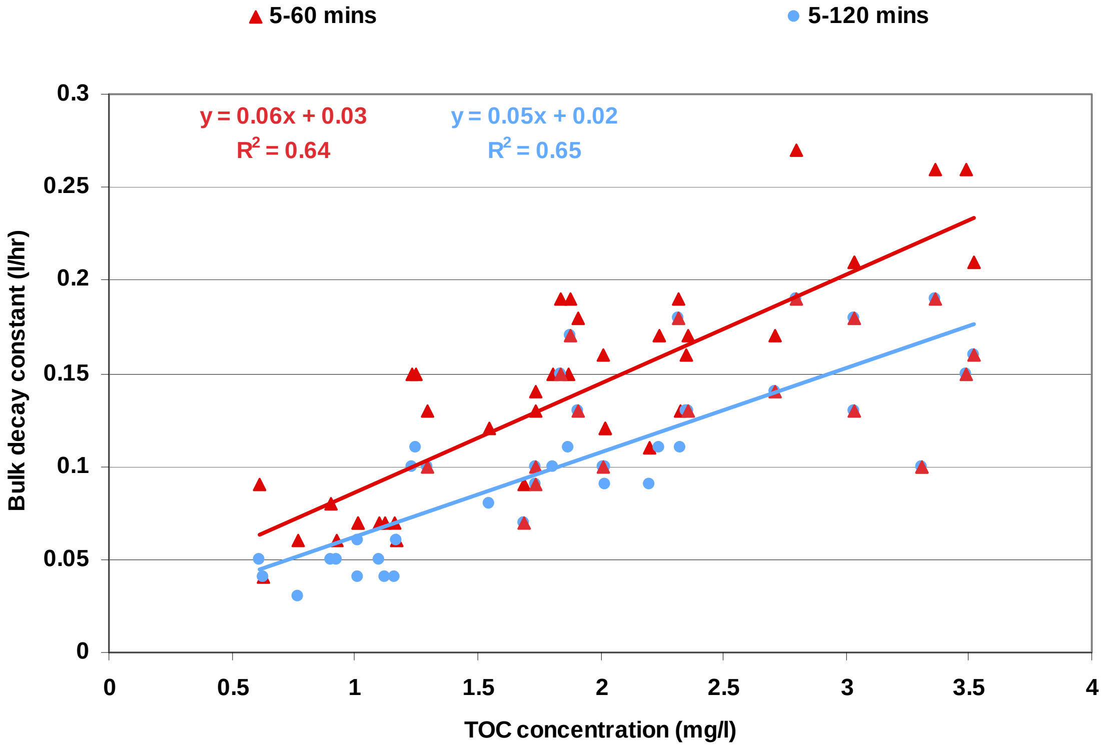


Figure 5.36; TOC concentrations vs. bulk decay constants between 5-60 minutes and 5-120 minutes for all six WTWs post-GAC tests conducted at 15 °C and an initial chlorine concentration of 1.7 mg/l.

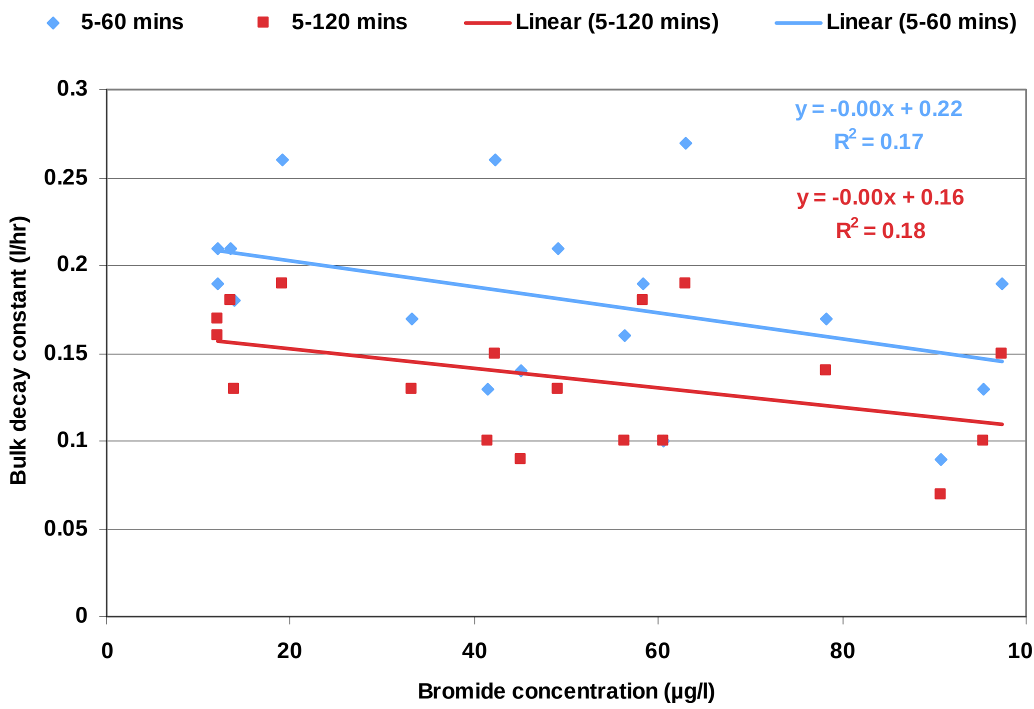


Figure 5.37; Post-GAC bromide concentration vs. bulk decay constants over 5-60 and 5-120 minute periods for all tests conducted at an initial chlorine concentration of 1.7 mg/l and temperature of 15°C at all six WTWs.

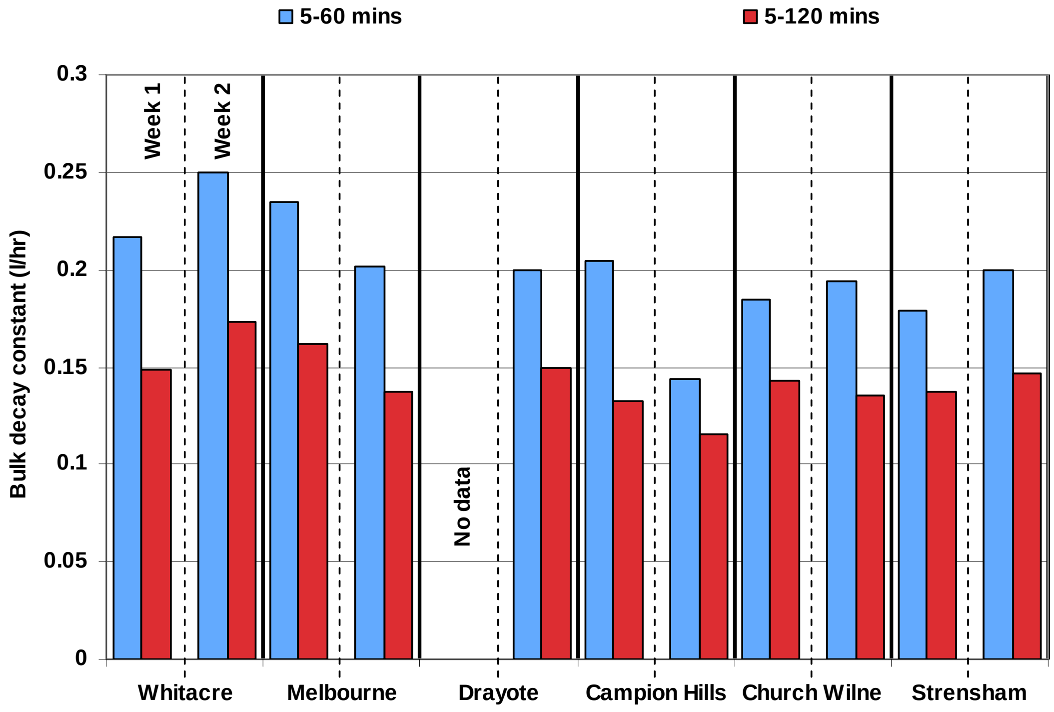


Figure 5.38; Average bulk decay constants from the 7 post-GAC variation tests at the six WTWs (portayed in Figures 5.33 – 5.35) (between 5-60 and 5-120 minutes).

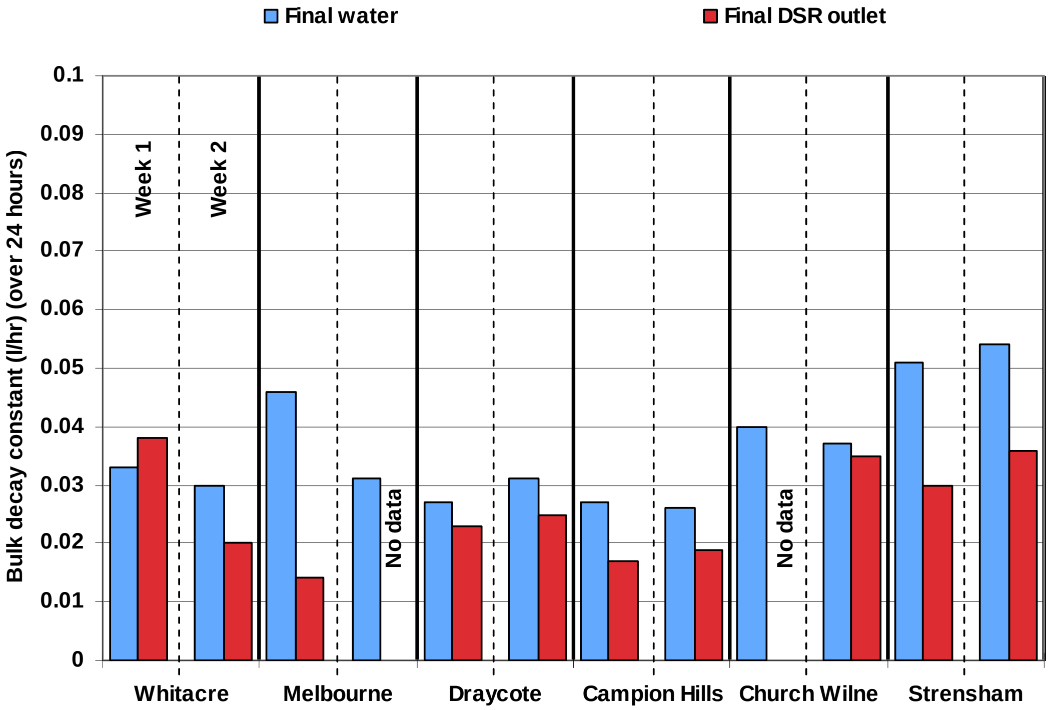


Figure 5.39.; Bulk decay constants over 24-hours for final water tests at each of the six WTWs and final DSR outlet water on two summer 2007 sampling weeks.

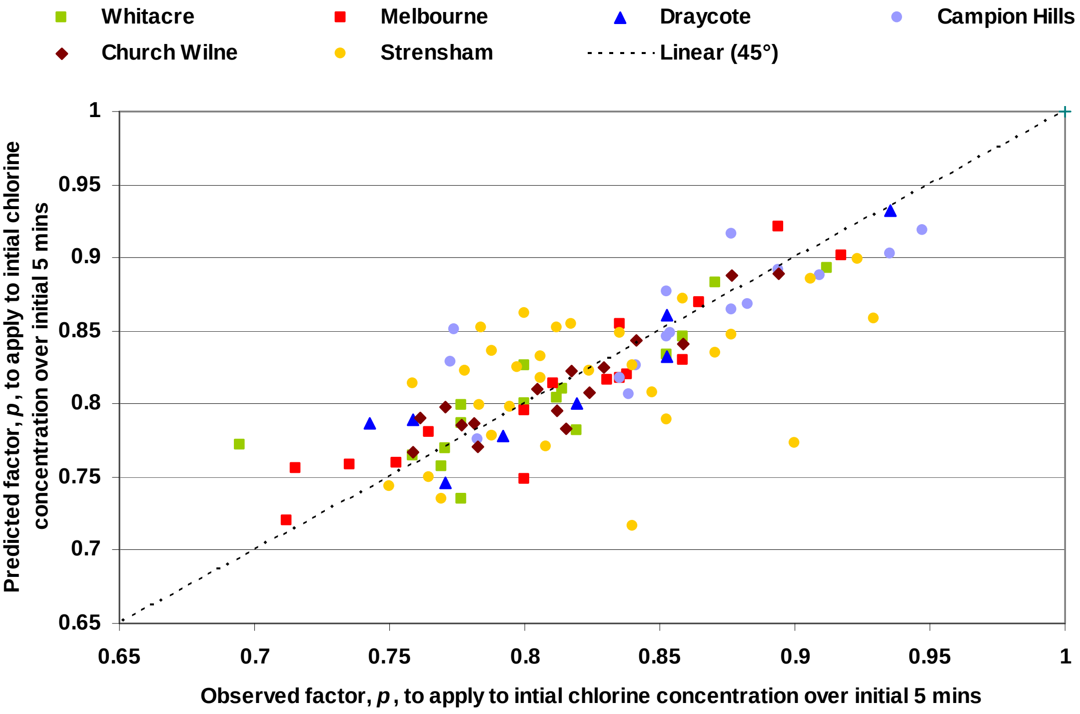


Figure 5.40; Observed vs. predicted factors (*p*) to apply to initial chlorine concentration to represent drop in free chlorine concentration (calculated via stepwise regression). 45^o line (dotted black line).

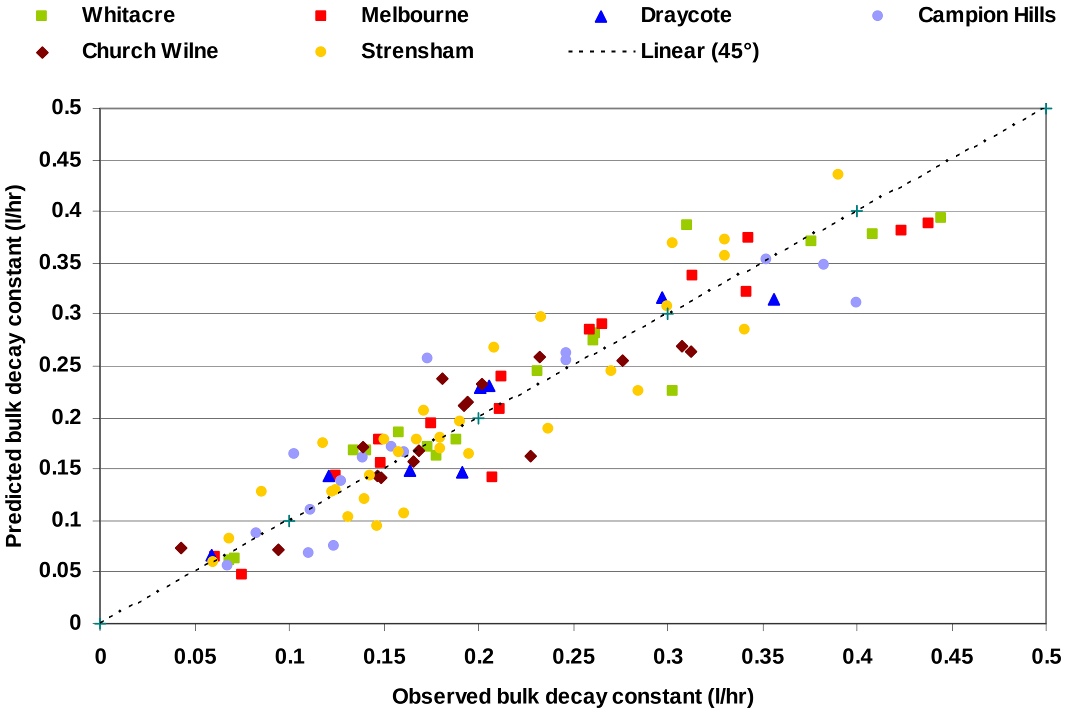


Figure 5.41; Observed bulk decay constants vs. predicted bulk decay constants (calculated via stepwise regression) between 5-60 minutes. 45° line (dotted black line).

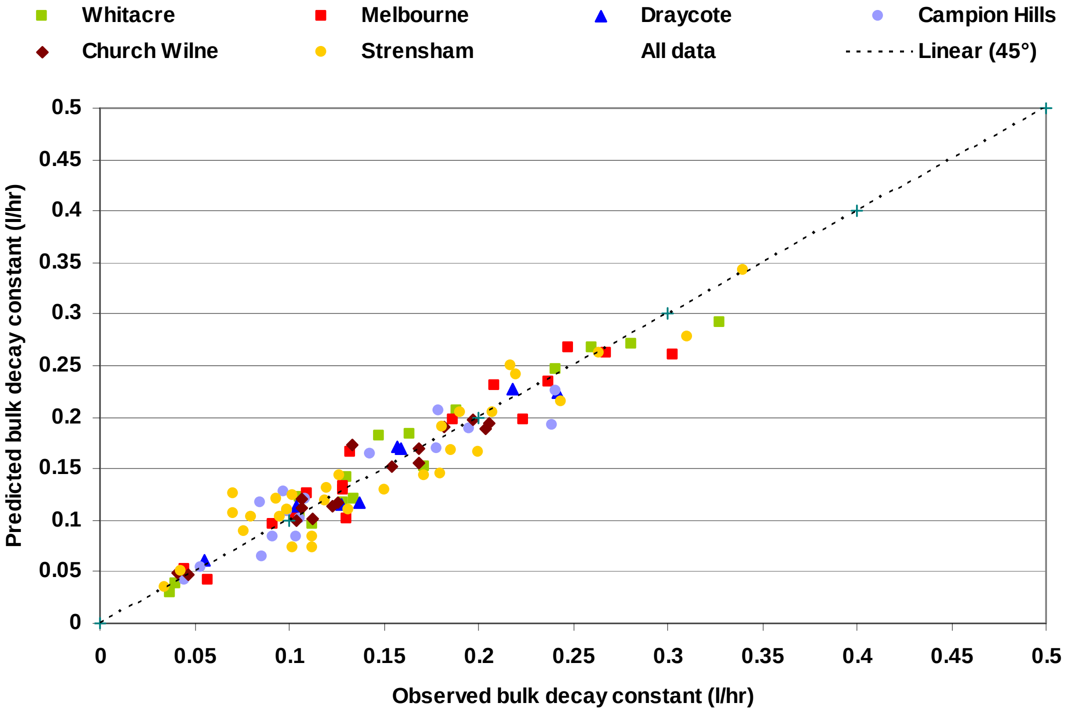


Figure 5.42; Observed bulk decay constants vs. predicted bulk decay constants (calculated via stepwise regression) between 5-120 minutes. 45° line (dotted black line).

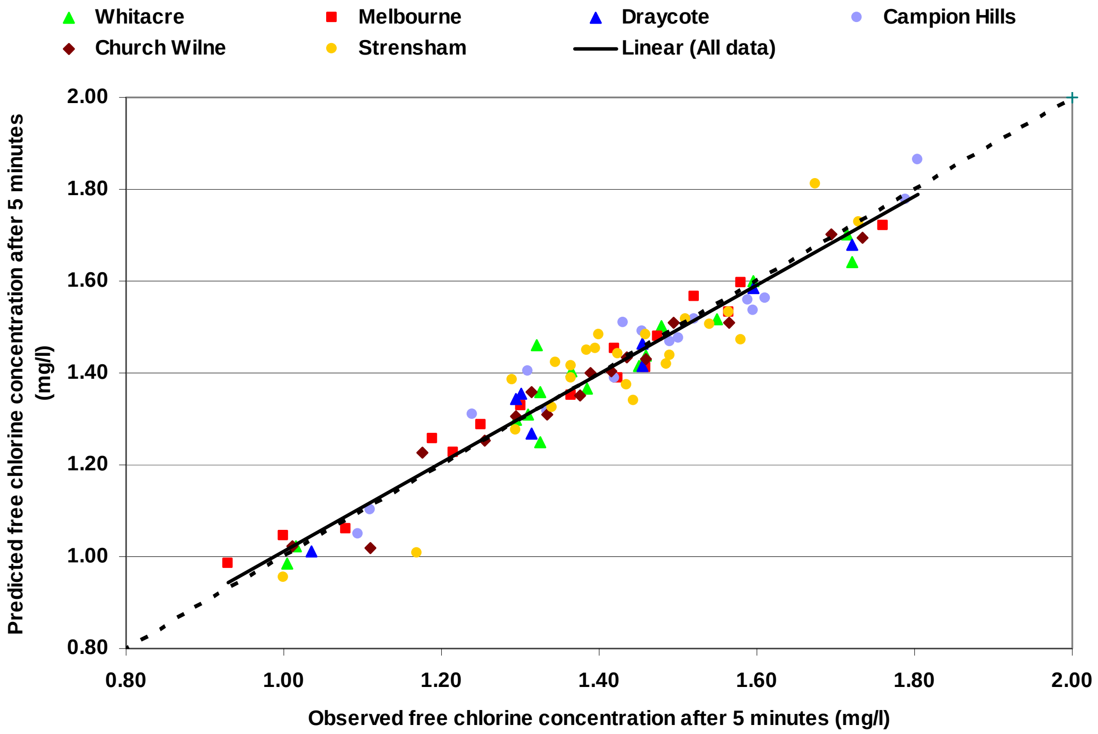


Figure 5.43; Observed versus predicted free chlorine concentrations after 5-minutes using predictive equations.

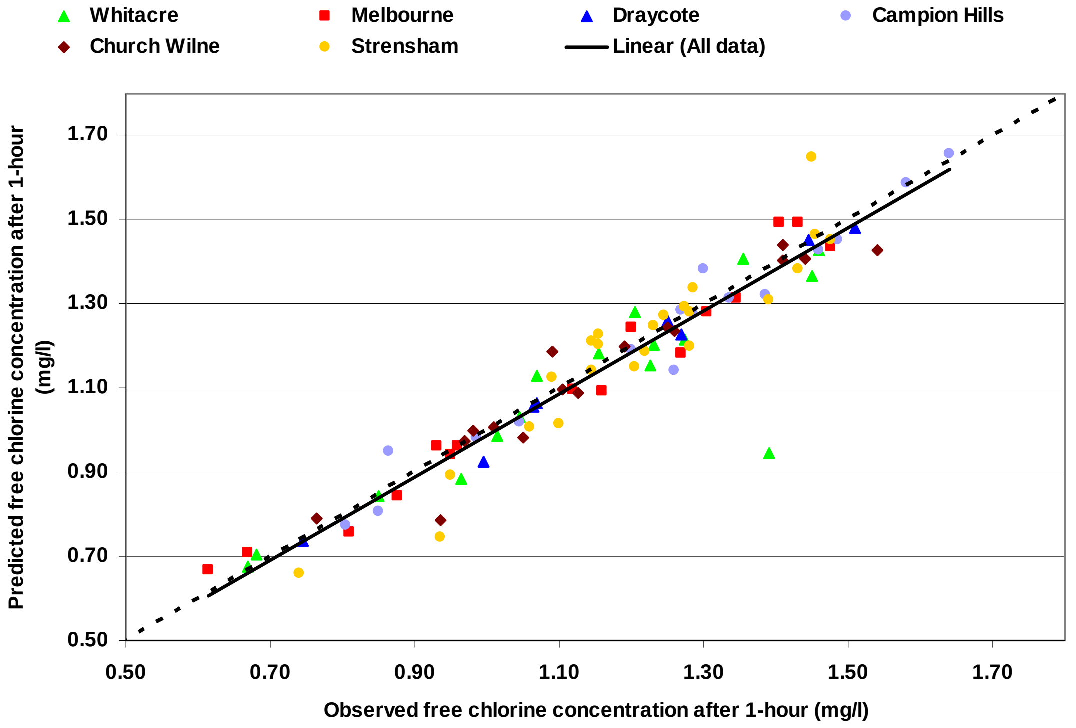


Figure 5.44; Observed versus predicted free chlorine concentrations after 1-hour using predictive equations.

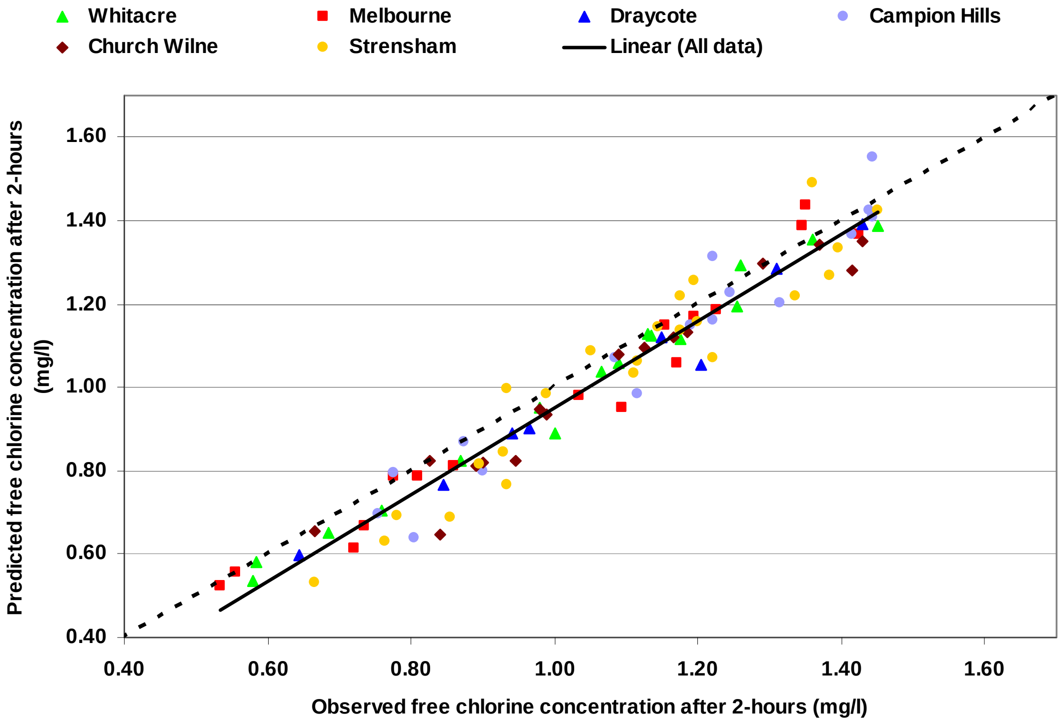


Figure 5.45; Observed versus predicted free chlorine concentrations after 2-hours using predictive equations.

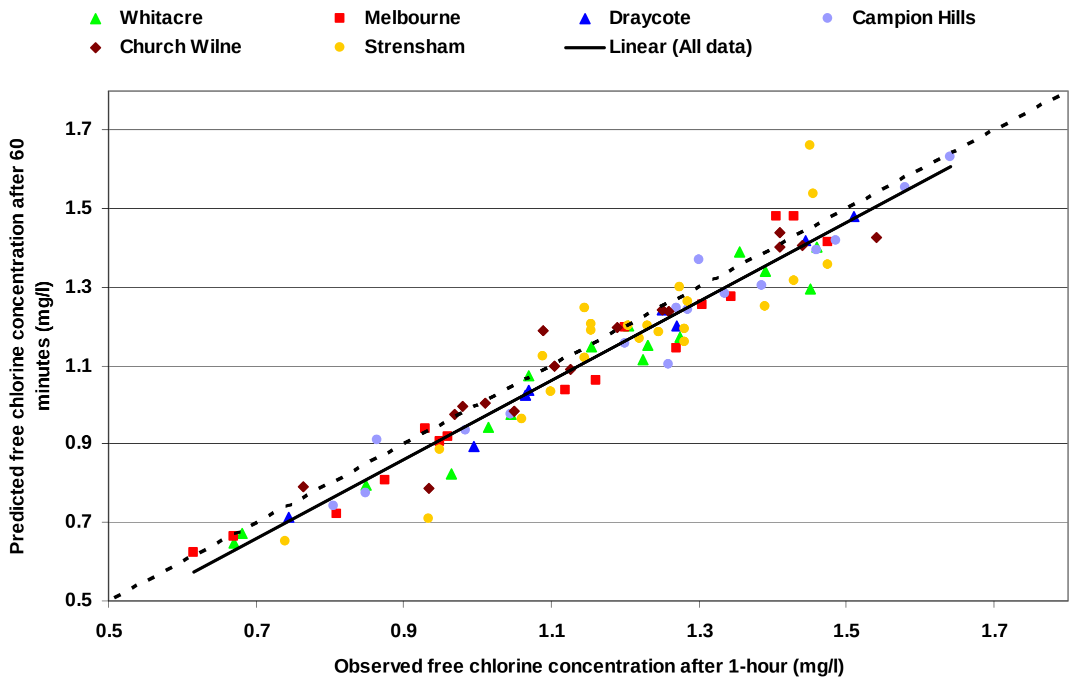


Figure 5.46; Observed versus predicted free chlorine concentrations after 1-hour using predictive equations (using the best fit line constrained through ln(C_{5mins}) method.

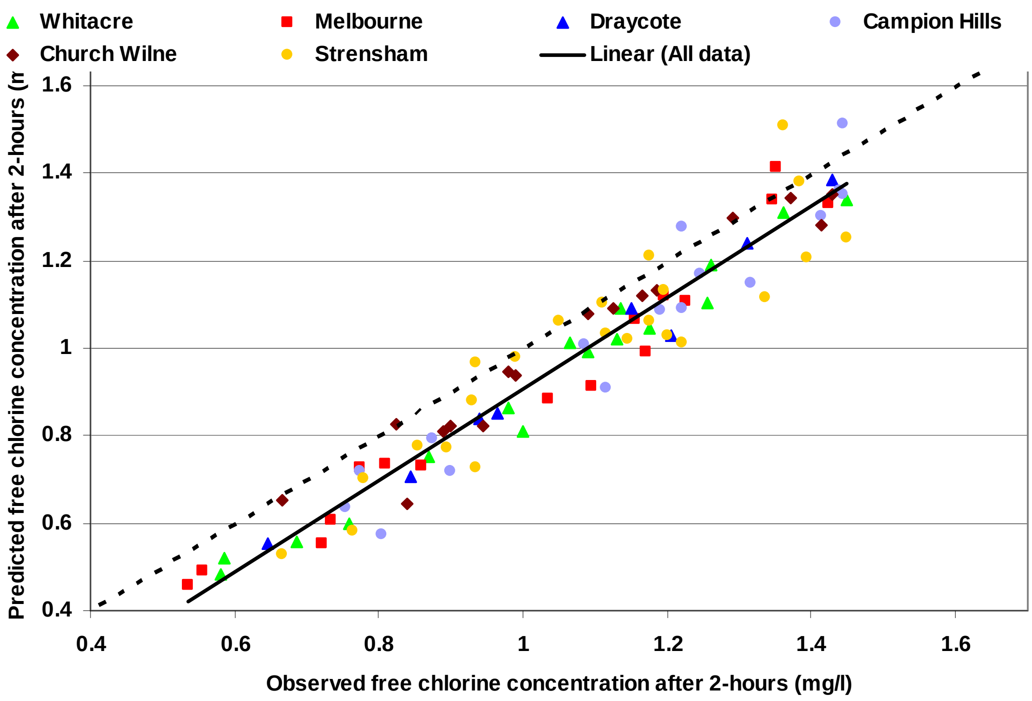


Figure 5.47; Observed versus predicted free chlorine concentrations after 2-hours using predictive equations (using the best fit line constrained through ln(C_{5mins}) method.

Chapter 6 THM Productivity

6.1 Introduction

This chapter presents experimental results of THM formation through each of the six WTWs and their respective distribution systems. The qualitative influence of the initial chlorine concentration (C_0), TOC concentration, contact time, temperature, and bromide concentration on THM formation is discussed. A practical and cost effective approach to model THM formation in relation to the chlorine consumed (relative to the above parameters) is then presented and its implications examined.

The work in this chapter focuses on objective (iii) from Chapter 1;

- ***To investigate THM formation in relation to key water quality parameters, initial chlorine concentration, temperature, contact time and water treatment unit and supply processes, and consequently to determine appropriate THM formation models.***

6.2 Test details

To allow for the temporal and environmental aspects of THM formation to be assessed, a total of 278 THM and 168 bromide measurements were taken at specified time intervals (stated in section 3.2.3) during the chlorine bulk decay tests detailed in the preceding chapter. Used in conjunction with spot samples taken on both this study’s sampling days and in routine STW sampling, a quantitative analysis of THM formation has been undertaken.

The kinetics of THM formation are complex and are influenced by numerous factors (section 2.10). To facilitate the investigation of the influence of initial chlorine concentration (C_0), temperature, TOC and bromide concentration, THM measurements were taken after each of the two-hour bulk decay experiments where one of these parameters was varied whilst others were fixed (as described in section 5.6.2).

To allow for the temporal variation of THM formation to be assessed in greater resolution, more frequent samples were taken during tests on selected post-GAC (over 4 hours) and final water tests (over 24 hours), to represent THM formation across the contact tank and in the distribution system, respectively. Details of the frequency and timing of these samples is provided in Table 4.1 and are described in more detail in section 3.2.3.

Again, the majority of this chapter’s analysis will focus on Strensham WTW, with the remaining five WTWs being referred to in a comparative analysis towards the end of the chapter.

6.3 Differences with cited literature

Most previous studies have either concentrated on the control of THM formation either at the WTW (Jacangelo *et al.,* 1995; Volk *et al.,* 2000; van Leeuwen *et al*., 2005; Uyak *et al*., 2005; Hong *et al*., 2007; Chen *et al*., 2008; Teksoy *et al*., 2008) or in the distribution system (Golfinopoulos *et al*., 1998; Elshorbagy *et al*., 2000; Rossman *et al*., 2001; Rodriguez *et al*., 2004; Toroz & Uyak, 2005; Baytak et al., 2008; Chaib & Moschandreas, 2008), treating the two as separate elements. Many of these studies have attempted to model THM formation using either stoichiometric expressions or empirical models that require a large amount of sampling data and knowledge of the hydraulics within a system. This study aims to explore THM formation from the raw water to customer tap, linking THM formation directly to no parameter other than chlorine decay, following the concept suggested by Moore *et al*. (1994), Clark (1998), Clark & Sivagnesan (1998) and Hua (2000). The underlying influences of the variation of C_0, TOC, bromide, temperature and time on this relationship is explored, therefore allowing for a more rigorous assessment of its merit than in previous studies.

Previous studies on STW systems have investigated THM formation where pre-chlorination was practised and thus the water was exposed to chlorine at a stage where little or no treatment had previously occurred. This study investigates THM formation under conditions of no pre-chlorination. This reflects the preferred operational trends that are prevalent in most WTWs in water supply systems in the STW catchment and also throughout the developed world.

6.4 THM formation through the WTW

Section 4.5, demonstrated that approximately 50 % of the total quantity of THM formed by the end of the Strensham distribution system has been formed by the time the water enters the distribution system (*i.e.* 50 % of TTHM found at customer tap is formed in the WTW). In contrast to operational practices in the distribution system, where adjustments are restricted by, for example, the management of microbiological risks or expensive capital improvements, cost effective changes may be made to operational practices through the WTW that may be beneficial to a range of treatment aims, including the reduction of THM formation. An understanding of the formation of THM in WTWs is therefore an integral part of a strategy for THM management under both present and potential future water treatment operational practices.

THM concentrations formed after the two-hour bulk decay tests at the various sampling points through Strensham WTW on the different sampling days are shown in Figure 6.1 (each test conducted at a C_0 of 1.7 mg/l and a temperature of 15 °C). Similar to the decline in bulk chlorine decay constants (Figures 5.5 & 5.6), the amount of THM formed through the WTW decreased with treatment, indicating the removal of potential THM precursor material with each subsequent treatment process. From the raw water sampling point, there were successive declines of 20 %, 9 % and 16 % in the amount of THM formed following the clarification, filtration and GAC unit processes, respectively. The greatest reduction once again occurred across the clarification process (6.8 µg/l reduction between average raw and post-clarifier samples), however the GAC adsorption process also accounted for a significant reduction in TTHM formation (with a 5.3 µg/l reduction between average inlet and outlet concentrations).

Previous studies have reported GAC to be effective at removing THM precursors which coagulation and filtration are unable to, as it is known to remove smaller NOM molecules (Speth, 2001; Roberts, 2004; Babi *et al.*, 2007). However, process management (such as the bed age / regeneration rate) has been shown to influence its efficacy significantly (Hooper *et al.*, 1996; Coutis, 2003; Roberts, 2004; Babi *et al.*, 2007; Kim & Kang, 2008).

Considering the modest quantities of organics involved in the formation of THM (*e.g.* to form 100 µg/l of chloroform requires approximately 10 µg/l of carbon), the positive relationship between concentrations of TOC and TTHM formed through the WTW was reasonable, displaying an R^2 value of 0.60 (significant at the 1% level) (Figure 6.2). Although TOC is a direct surrogate measure of a water's organic carbon content, it is not necessarily a consistent measure of DBP precursor concentrations. One explanation given for this is that TOC does not provide an indication of the aromaticity, aliphatic nature, functional group chemistry, or chemical bonding associated with natural organic molecules (USEPA, 1999), all of which are of significance when determining THM productivity (Reckhow *et al.*, 1990; Singer, 1999; Drikas, 2003; Reckhow *et al.*, 2004; Uyguner *et al.*, 2004). The reactivity of the chemical bonds and functional groups is likely to be a significant factor in explaining why different waters through the WTW with similar TOC concentrations formed different TTHM concentrations under similar test conditions.

Figure 6.3 verifies the positive relationship between the concentrations of TOC and TTHM formed at the raw and post-GAC sampling points (R^2 values of 0.54 and 0.47 respectively, both significant at the 2 % level). Interestingly, TTHM formation at the post-GAC stage was higher on the two summer 2007 sampling days than the tests conducted during the Spring months, even though all tests were conducted at 15 °C. Although TOC concentrations were also higher on these two sampling days (average ~ 2.68 mg/l) compared to the Spring sampling days (average ~ 1.83 mg/l), it is also likely, that the chemical matrix of the water will vary through the year leading to the water being more reactive at different times of the year (*e.g.* due to the seasonal variation in surrounding land use / vegetation etc.). This is of concern as temperature and bromide are also typically at their highest during the summer months at Strensham WTW (as detailed in Chapter 4). It would be anticipated that the THM concentration would increase with larger concentrations of bromide present in the water. However, no perceptible relationship was observed between raw and post-GAC bromide concentrations and the amount of TTHM formed for the conditions observed (Figure 6.4).

A change in the relative quantities of the four main THM species (Figure 6.5) was observed through the WTW. There was a significant shift from chloroform being the predominant species at the start of the WTW (with an average of 78 % of TTHM in the raw water samples) to the brominated species gaining in relative magnitude through the subsequent treatment processes (by the post-GAC samples, chloroform only accounted for an average of 38 % of TTHM). This is linked to the observations made in section 4.4, where treatment processes were shown to significantly remove organics whilst not appreciably reducing bromide concentrations, thus altering the bromide : organic carbon and bromide : chlorine ratios, which effect the relative formation of brominated DBPs (Summers *et al*., 1993; Ichihashi *et al*., 1999; Sohn *et al*., 2006).

A dimensionless term useful in evaluating the complex role of bromide in the aggregate speciation of a given water sample is the bromine incorporation factor (BIF) (section 2.10.4).

This term, defined by Gould *et al*. (1981), is the molar THM concentration as bromide divided by the total molar THM concentration:

$$N = \frac{\sum_{n=0}^{3} n(CHCl_{3-n}Br_n)}{\sum_{n=0}^{3} CHCl_{3-n}Br_n} \qquad (2.23)$$

As a result of carbon removal and bromide conservation, the BIF increased through the WTW from a value of 0.28 in the raw water to 1.09 by the post-GAC stage (Figure 6.5). As bromine (atomic mass ~ 79.9) is approximately two times the mass of chlorine (35.5), an increase in BIF will result in an increase in THM, even (potentially) if there is a decrease in the available carbon. The BIF values after the post-GAC sampling point remained steady through the remainder of the WTW and into the distribution system, as the influential factors determining organics and bromide concentrations stabilized.

Where bromide concentrations were consistently measured in conjunction with the bulk decay tests (raw and post-GAC waters), a positive relationship between bromide concentrations and BIFs was observed (Figure 6.6). The relationships were weakened due to the numerous external influences (R^2 values of 0.46 and 0.40, significant at the 3 % level), but correspond to the similar observations in chapter 4 between raw water bromide concentrations and the speciation of final water THM concentrations (Figure 4.38).

Analysis from all bulk decay tests conducted on post-GAC waters showed that waters with high bromide concentrations tended to have a higher fraction of brominated species as a percentage of TTHM and higher BIFs, whereas waters with a low bromide and high TOC concentration had a higher fraction of chloroform as a percentage of TTHM species and lower BIFs (Figure 6.7). On the whole, increasing the bromide : TOC ratio increased the proportion of brominated THMs and the resultant BIF (Figure 6.8), which is in agreement with previous findings (Amy *et al*. 1991; Rathburn, 1996; Roberts, 2004; Sohn *et al*. 2007). However, as displayed in Figure 6.7, there were noticeable exceptions. For example, the tests conducted on the 21st February and the 4th March 2008, each exhibit the same TOC concentrations (1.74 mg/l) but the bromide concentration on the latter sampling day was approximately half that of the former. The difference in the bromide : TOC ratio is not reflected in the relative distribution of THM species and BIF, which were practically the same on both sampling days, thus highlighting the complexities of the reactions taking place.

6.5 Contact tank simulation

Similar to the modelling of chlorine decay, specific emphasis was placed on quantifying THM formation across the contact tank. Spot samples taken through the WTW demonstrated that approximately 77 % of the total amount of THM formed across the WTW occurred within the contact tank. Also, since the suspension of pre-chlorination at each of the studied WTWs, primary chlorination now occurs at this stage.

6.5.1 Variation with independent parameters

To facilitate investigation of the influence on THM formation of $C_{0,}$ temperature, bromide and TOC; THM and bromide measurements were taken at the conclusion of each of the two-hour bulk decay experiments (on post-GAC water), varying one parameter whilst others were fixed. The results from the two summer sampling weeks' tests at Strensham WTW are summarized in Figure 6.9.

Temperature (Θ) Similar to the strong relationship observed at Strensham WTW final water between ambient temperature and TTHM concentrations (Figure 4.30), a 20 °C rise in temperature led approximately to a 50 % increase in the amount of TTHM formed in tests on matching waters.

Initial chlorine concentration (C_0) Increasing the chlorine dosage resulted in an increase in the amount of TTHM formed, with an increase of approximately 5 µg/l between a C_0 of 1.3 mg/l and 2.1 mg/l. The variation of C_0 did not have such a profound effect as the variation of temperature, although it is probable that far smaller quantities of THM would have been formed at very low initial chlorine concentrations outside of the tested range (that are not representative of typical concentrations at the contact tanks studied in this investigation).

Sample water dilution Interestingly, THM formation did not change significantly between the tests at different dilutions of sample water, with the averages of the three tests all being within 4 µg/l of each other. This is curious, as one would expect the amount of THM precursors in the water to be reduced by similar factors to the dilution, as there are no processes selectively removing certain fractions of the organic and inorganic matrix (which would have an influence). The dilution method exchanges only a fraction of the total volume of sample water, therefore leaving a quantity of (albeit reduced) fast reacting precursors remaining in the fraction of sample water, which could contribute to the disproportionately high concentration of THM formed over the relatively short test period. Over an extended contact time it would be anticipated that the effects of the dilution method on THM production would become more apparent, as the total (both fast and slow reacting) precursor concentration will contribute to THM formation.

Speciation of THM The differences in THM speciation and BIF as a result of the variation in bulk decay test conditions are shown in Figures 6.10 and 6.11. In general, it was observed that the decline in bromide concentrations over the 2-hour test period was greater for higher C_0 and temperatures (shown by the bold red values at the top of plots). The decrease in C_0 and increase in temperature also led to a slight increase in the percentages of brominated THM species and BIF. This is in agreement with similar findings by Rathburn (1996) and Roberts (2004) in their studies of the variation of BIF with C_0 and temperature, respectively. An increase in sample water strength of dilution resulted in a significant decrease in the percentage of TTHM that was chloroform and a increase in BIFs. Although the modest increase in BIF is accentuated by the scales chosen in Figures 6.10 and 6.11, it suggests the bromide effect outweighs the carbon effect in this process. The lower percentages of brominated species observed on the second sampling week compared to the first sampling week may be attributed to the slightly lower bromide concentrations and the 30 % increase in TOC concentration.

6.5.2 Characterising temporal variation of THM formation

One of the key factors in THM formation is the time during which a particular disinfectant remains in contact with the precursor material (section 2.10). THMs are typically chlorination end products, therefore increasing the reaction time will lead to an increase in the amount of THMs produced. This was demonstrated in the experiments at ambient conditions over a 4-hour period at Strensham WTW where more frequent samples were taken (Figures 6.12 and 6.13).

Mirroring the decay of chlorine, the rate of THM formation was initially rapid, followed by a declining rate. It was observed that between 39 % and 47 % of the total amount of THM formed over 2-hours of the test occurred within the initial five-minutes of the tests. This rapid formation has been observed in previous studies (Koch *et al*., 1991; Singer, 1999; Chowdhury & Amy, 1999, Kruithof *et al*., 1999; Gang *et al*., 2003; Courtis, 2003; Jegatheesan *et al*., 2008; Fabbricino & Korshin, 2009). Previous workers (Kruithof *et al*., 1999; Courtis, 2003; Fabbricino & Korshin, 2009) explained this by suggesting the presence of fast and slow reacting THM precursors contained within the organic matrix of water, with the faster reacting precursors being preferentially oxidised.

The rate of bromide consumption was also initially rapid followed by a declining rate, demonstrating the interdependence between the three parameters. After two hours there was a 36 % (21.1 µg/l) and 51 % (22.8 µg/l) drop in the initial bromide concentrations on the first and second sampling weeks, respectively.

6.6 Modelling THM formation

Numerous attempts have been made to describe the mechanisms of THM formation and kinetics (Trussel *et al*., 1978; Amy *et al*., 1987; Clark & Sivaganesan, 1998; Hua, 1999;

Roberts, 2004; Uyak *et al*., 2005; Hong *et al*., 2007). Due to the complexity of the reactions between the organic matrix and halogenated compounds there are, to date, no accurate analytical-mechanistic models of THM formation, with the majority of existing models developed from either overall reaction sotichiometry expressions or empirical equations derived from linear and non-linear regression analyses (section 2.11).

Empirical models can lack precision because the formulae developed are restricted by the conditions under which the experimental data are obtained, leading to a reliance on costly data collection and analysis. Consequently, there remains the need for a simple, yet robust means to predict THM formation under variable raw water quality and operational conditions in WTWs and distribution systems.

6.6.1 The K_{TC} value concept

This study adopts a pragmatic empirical model, which can overcome some of the problems of more multifaceted empirical formulae described in chapter 2. Following an approach used by Hua (1999), THM formation is linked solely with the overall reaction of chlorine with precursors in the water. This is represented by the coefficient of proportionality, K_{TC}, in the following expression;

$$THM = THM_0 + K_{TC}(C_0 - C) \qquad (6.1)$$

Where THM_0 and C_0 are the initial THM and free chlorine concentrations respectively, THM and C are the THM and free chlorine concentrations at time, t, and the coefficient of proportionality, K_{TC}, has the units µg/l THM per mg/l free Cl.

If the initial concentration of THMs is zero, then Equation (6.1) becomes;

$$THM = K_{TC}(C_0 - C) = K_{TC}\Delta C \tag{6.2}$$

This approach substitutes the convoluted inter-relationships between independent parameters and THM formation with mass relationships, incorporating all reactants and influential factors within the coefficient of proportionality. While this approach potentially compromises accuracy, it essentially provides an expedient basis for modelling THM formation in operational circumstances where practical and cost considerations are paramount. As units and working definitions are universal it also allows for a relatively straightforward comparison between the potential reactivity of different waters.

The coefficient of proportionality (K_{TC} value) in equation 6.2 can be approximated graphically by the gradient of the best-fit line though the correlation between THM formed due to the amount of chlorine consumed. As the concept employs first-order kinetics, it dictates the best-fit line to be a straight line that passes through the origin and the centroid of the data, as when no chlorine is consumed, it is improbable that any THM could be formed. This implies the line takes the form $y = mx$, where y is the concentration of THM formed, x is the amount of chlorine consumed and m is the K_{TC} value.

Figure 6.14 shows a scatter plot of the chlorine consumed versus THM formed at different time intervals over the four-hour tests at ambient conditions (using the same data from Figures 6.12 and 6.13). Two best-fit straight lines are shown on the plot for each of the sampling days, with one fitted through the origin, and the other not constrained though the origin (dashed line).

The two dashed lines take the form of $y = ax + b$, where b is the y-intercept. Both represent good correlation to the data, with R^2 values of 0.98 and 0.99 (significant at the 1 % level) on the first and second sampling days, respectively. Taking this form however requires the determination of two constants, which adds complexity to the process and invalidates the use of an accurate proportionality coefficient, K_{TC} value. With the y-intercepts (*b*) on both lines being close to the origin (-1.31 µg/l and -0.20 µg/l), and the gradient of each of the lines being comparable to the gradients of the equivalent lines passed through the origin, it suggests that constraining the correlation such that the line of best fit passes through the origin does not deteriorate the relationship significantly, and is fit for purpose.

Interestingly, a similar plot showing the relationships between bromide consumption and THM formation (Figure 6.15) follows a similar pattern to the trend with chlorine, albeit with weaker statistical correlation (R^2 values ranging from 0.84 to 0.93, significant at the 1 % level).

Section 6.5.2 illustrated the presence of fast and slow reactions in both the formation of THM and the consumption of chlorine and bromide. The application of a ‘constant’ in the adopted approach suggests that different K_{TC} values would be required to account for these temporal differences in kinetics. However, as Figures 6.14 and 6.15 demonstrate, the concomitant rapid THM, chlorine and bromide kinetics in the initial stages, followed by a declining rate with time, appear to compensate each other, leading to the high accuracy of fit in the linear trend lines. This suggests that the application of a constant K_{TC} value with time is valid for a given water, over a known time period where the temporal change in a water's THM productivity is accounted for by the preceding calculations incorporating the kinetics of chlorine decay.

K_{TC} values for all post-GAC water tests (calculated by the THM formed and chlorine consumed over two hours) suggest an average of 39 µg/l TTHM per mg/l free Cl (s.d. ~ 16.3) over a two hour period (see Table 6.1 for determination). With the omission of the sample water dilution tests, which as explained in section 6.5.1, showed THM formation to be unpredictably high, this average reduced to 34 µg/l TTHM per mg/l free Cl (s.d. ~ 7.6). Both values are very close to the observed value calculated at different time periods through the longer 4 hour ambient conditions tests (depicted in Figure 6.14), but are slightly lower than the observed values at three other STW WTWs (Hua, 2000, K_{TC} ~ 45 µg/l TTHM per mg/l free Cl). This is most likely due to the differences in raw water characteristics and operational conditions between the studies, and the differences in test conditions.

6.6.2 Predictive equation

In a similar manner to the chlorine decay results (section 5.6.3), the calculated K_{TC} data from all the tests on post-GAC water (excluding the dilution tests) were collated through stepwise regression (using SPSS) to develop an equation for predicting K_{TC} values, relative to inputted $C_{0,}$ temperature, TOC and bromide concentrations, taking the form:

$$K_{TC} = A + (a \cdot C_0) + (b \cdot \Theta) + (c \cdot TOC) + (d \cdot Br) \quad (6.3)$$

Where:

C_0 = Initial chlorine concentration (mg/l)

Θ = Temperature (^{o}C)

Br = Bromide concentration (µg/l)

A, a, b, c, d = Constants determined by stepwise regression

Equation 6.3 relates the amount of THM formed to chlorine consumption under a variety of test conditions. The constants A, a, b, c and d are summarized in Table 6.2. Figure 6.16 shows the observed versus predicted K_{TC} values to be comparatively accurate, with the majority of predicted K_{TC} values being within 5 µg/l TTHM per mg/l free Cl (13.6 %) of the observed K_{TC} values (reflected by the proximity of the scatter of points around the 45° line), with the average difference being ± 4.6 µg/l TTHM per mg/l free Cl. The range of the predicted values is less than that of the observed values due to the averaging out of the random errors associated with the observed values.

6.6.3 Performance of the predictive equations

To assess its accuracy, the predictive equation was applied to a range of indicative operational values for each of the four individual parameters in equation 6.3, whilst fixing remaining parameters at their mean values. The results are displayed in Figures 6.17, 6.18, 6.19 and 6.20 for the variation of C_0, temperature, TOC and bromide respectively, along with the observed K_{TC} values, calculated from sampling day data.

An increase in C_0 leads to a decrease in the predicted K_{TC} values. This is in agreement with observations from laboratory tests, also shown in Figure 6.17. This possibly reflects the fact that of the total amount chlorine consumed during the reactions only a small fraction contributes to THM formation in comparison to the remaining by-products of chlorination. The increase in chlorine concentration (and subsequent consumption) therefore outweighs the corresponding increase in THM production, leading to the observed decline in K_{TC} values.

An approximate 30 % increase in the predicted K_{TC} values results from a doubling of the bromide concentration. As demonstrated earlier, an increase in bromide concentration will lead to an increase in BIF and, due to the brominated compounds being heavier than the associated carbon-chlorinated forms, an associated rise in the weight of TTHM. Statistical dependence between bromide concentration and THM from the observed data is weak however (R^2 value of 0.08, significant at the 15 % level).

A doubling of the TOC concentration once more leads to an increase of approximately 30 % in the predicted K_{TC} value. The inverse relationship between bromide and TOC concentrations in the source river at Strensham, highlighted in Chapter 4, suggests this to be counter intuitive, given the reasoning specified in the preceding paragraph. However, it could reflect the alteration of the carbon matrix with the seasonal effects in the river flow and unit processes management. The modest statistical dependence between the TOC concentrations and K_{TC} values, (R^2 value of 0.11, significant at the 10 % level) and also between K_{TC} values and chlorine and bromide, is most probably due to the complex, competitive and fluctuating interactions between bromide, chlorine and carbon in the relatively short time span of the tests.

The variation of temperature does not change predicted K_{TC} values significantly. Temperature was shown to play a significant role in both the formation of THM and chlorine decay and it is likely that the concurrent effects on both are relatively proportional, thus maintaining a constant K_{TC} value over the temperature range.

To test the applicability of using the K_{TC} approach to model THM formation with time, the predicted K_{TC} values determined by equation 6.3, were applied to each of the test conditions in combination with the two-stage chlorine decay modelling process developed in Chapter 5. The same K_{TC} value was applied to the chlorine consumed over different time periods through the entire test period (*e.g.* between 0-5, 5-10, 10-15 minutes etc.). An example of the predicted chlorine and TTHM concentrations over a four-hour test period is shown in Figure 6.21, with the actual observed concentrations from the same test conditions also shown. Prediction of TTHM in this example is reasonable with predicted and observed concentrations never being greater than 10 µg/l from the observed concentration over the 4-hour time period.

A similar procedure was applied for each of the post-GAC test conditions and a comparison between the observed and predicted THM concentrations after two hours is shown in Figure 6.22. In general THM concentrations were slightly over-predicted, although the predicted concentrations were usually within ± 5 µg/l TTHM (average of ± 3.9 µg/l or 13.8 %) of the observed concentrations.

6.6.4 Alternative means of calculating K_{TC}

K_{TC} values thus far have been calculated by the use of laboratory data, which on a routine basis is expensive and time consuming to collect and analyse. An alternative means of calculating K_{TC} values would be to utilise data already routinely monitored at the WTW. Unfortunately, THM concentrations at each of the studied WTWs are only monitored on a routine basis at the final water. Figure 6.23 portrays the relationship between final water THM concentrations at Stensham WTW with the decline in chlorine concentrations across the contact tank, based on STW samples taken on the same days between October 2006 and October 2008. The linear correlation between the points is reasonable (R^2 ~ 0.43, significant at the 1 % level) bearing in mind the large number of data points.

Interestingly, the line does not pass through the origin, which one would expect as no THM could be formed when chlorine consumption was zero. This could be due to chlorine consumption and THM formation being calculated over different spaces. It is likely that additional THMs are formed and extra chlorine consumed between the contact tank outlet and the final water, although by varying magnitudes due to the range of operational and environmental determinants that are not possible to determine accurately. However, this would only have the effect of changing the gradient of the correlating line, not the y-intercept. A more feasible explanation is due to the relative sampling and measurement accuracy of THM and chlorine concentrations at the WTW. The daily fluctuation of measured THM concentrations would be relatively small, as they would be dampened by contact tank hydraulics. Conversely, chlorine concentrations are likely to be considerably more variable due to the dosing and monitoring equipment being more erratic (amplified by samples being taken at two separate sampling points). The large variability of chlorine consumption (abscissa) and small variability in THM formed (ordinate) leads to the observed skewness in the fitted line away from the origin. Notwithstanding this, the regression line in Fig. 6.23 offers a cost effective route to calculating THM concentrations from routine monitoring data, with the gradient of the line (37.8) being similar to the calculated K_{TC} values from the laboratory tests, which averaged 39.1 (with the omission of the sample water dilution test data) (Table 6.4).

6.7 Distribution system

Previous studies have shown the occurrence of THMs in chlorinated water may vary significantly according to season and geographical location in the distribution system (Hallam, 1999; Rodriguez & Serodes, 2001; Courtis, 2003; Rodriguez *et al*., 2004; Baytak *et al*., 2008; Chaib & Moschandreas, 2008). Chapter 4 verified this variation in each of the six distribution systems (for example, in the Strensham to Shipston distribution system shown in Figures 4.40 & 4.41).

Temporal and spatial variability of THM concentrations will be caused by changes in the factors responsible for their formation and fate. However, comprehension of where, when and how they are formed is hampered by the experimental difficulties concerned with isolating independent parameters under a wide range of ambient water quality and operational conditions. There are also the additional problems associated with attaining detailed spatial access to the water that is predominantly supplied underground and stored in closed tanks.

To allow for a representation of THM, chlorine and bromide kinetics in the bulk phase of distribution system water, THM and bromide samples were taken at selected intervals during the 24-hour bulk decay tests on final waters and two locations in the Shipston distribution system (Table 6.1). A summary of the TTHM concentrations formed over the 24-hour test period on different sampling days at each of these locations is displayed in Figure 6.24. As with chlorine consumption, the extent of THM formation will be largely dependant on the ambient conditions of the tests, but similar to the observed bulk decay constants, the amount of THM formation can be seen to decrease as the water progresses through the distribution system. Average concentrations formed over the 24-hour test period decreased from 11.6 µg/l TTHM to 6.7 µg/l TTHM between the final water and Tysoe DSR outlet water samples. The latter average would probably be lower than it is as two Spring sampling days included in final water calculations are not included at Tysoe due to sampling and analysis errors.

TTHM concentrations taken over a finer temporal scale during the 24-hour test periods on the two summer 2007 sampling days on the final water are shown in Figure 6.25. Similar to the tests on post-GAC water, the rate of THM formation was again rapid initially, followed by a declining rate. Approximately 70 % of the total THM formed over 24-hours was produced in the initial 8-hours.

The amount of THM formed by different times corresponds reasonably well to the observed concentrations in both the concurrent spot samples taken on sampling days, and the historic STW concentrations, at similar travel times downstream of the final water. For example, concentrations after 8 hours (45.5 / 47.9 µg/l TTHM) are reasonably close to the observed concentrations on the corresponding sampling days (47.9 / 43.7 µg/l TTHM) at Oversley

Green BPS inlet, which is approximately 8.5 hours downstream of the WTW final water. On the whole, however, corresponding concentrations in the laboratory tests tend to be slightly lower than the observed spot samples. This is probably due to different numbers of data points, but might suggest the amount of THM formed in the distribution system is influenced by potential reactants found on the pipe wall surfaces or, more plausibly, due to the effects of continuous agitation of the water in transport, providing replenishment of the interface between chlorine and precursor material.

On both sampling days the pathways of THM formation with time are similar. The larger concentrations observed on the second sampling week (red line) are likely due to the slightly higher temperature, initial chlorine and TOC concentrations. The kinetics of the four individual THM species was similar (monotonic) to that of TTHM formation over the 24-hour test periods. Speciation of THM and BIFs also remained fairly consistent in the tests conducted on different waters through the distribution system (Figure 6.5), resulting from the negligible variation in organic and bromide concentrations observed in the distribution system in Chapter 4.

Similar to the WTW tests, the scale of THM formation was observed to be positively related to temperature, with concentrations from the summer tests being approximately double the equivalent concentrations formed in the Spring tests. Figure 6.26, shows the positive relationship between the two parameters to be stronger at the final water (R^2 value ~ 0.82, to a level of 1 % significance) in comparison to Oversley Green BPS outlet (R^2 value ~ 0.63, to a level of 1 % significance) and Tysoe DSR outlet (R^2 value ~ 0.50, to a level of 5 % significance). This possibly reflects the increasing disparity across sampling days between external factors such as previous chlorination and THM formation history at points further through the distribution system. No significant relationships were observed between final water TTHM concentrations and C_0, TOC and bromide concentrations (Figures 6.27, 6.28 and 6.29, respectively), although variation of these three parameters is not as substantial as temperature, due to WTW operational targets for the final treated water.

K_{TC} values were calculated using the chlorine consumed and THM formed in the final water and distribution system bulk decay tests, in a similar manner to the WTW bulk decay tests (Table 6.1). Calculated K_{TC} values (µg/l TTHM per mg/l free Cl) averaged 50.4 (s.d. ~ 18.6) at the final water, 59.4 (s.d. ~ 15.6) at Oversley Green BPS outlet, and 103.4 (s.d. ~ 37.9) at Tysoe DSR outlet. The large variability in values can be attributed to the wide range of ambient test conditions and the differences in water quality. As observed in previous studies (Hua, 1999; Courtis, 2003), it would be anticipated that K_{TC} values would decline through the distribution system to reflect the reduction in a water's reactivity as it passes through more rechlorination points. It is unclear why a different trend is observed here. One possibility is the problem with calculating K_{TC} values with relatively small amounts of chlorine consumed to comparatively large amounts of THM formed, which become more exaggerated towards the end of the system. K_{TC} values are intended to be used in conjunction with the chlorine decay work described in Chapter 5 in the modelling section of this study and will be considered in more detail in Chapter 7.

6.8 Inter-comparison of 6 WTW and parts of their distribution systems

A summary of THM results from tests on raw, post-GAC, final and DSR waters, at each of the studied WTWs is provided in Table 6.3.

No significant relationships were observed between WTW raw waters with high organic or bromide concentrations and WTWs with high concentrations of TTHM formed over the 2-hour bulk decay tests on raw water (Figure 6.30). Free chlorine concentrations at the end of the two-hour tests were however, low or below detection limits, indicating the tests were chlorine limited and the likelihood of further THM formation at higher dosages of chlorine and longer contact times.

Similar to the observations at Strensham WTW, THM formation was observed to increase with C_0, temperature and strength of sample water dilution at each of the WTWs (Figures 6.31 – 6.33). As with bulk decay constants, the effect of temperature was more pronounced on THM formation with the 10 ºC increase between 15 ºC – 25 ºC compared to the lower temperature change. This helps to justify the significant rise in both chlorine consumption and THM formation between the spring and summer months at each of WTWs (Figure 4.1). Again, sample water dilution did not lead to a significant change in the amounts of THM formed over the two-hour test period.

TTHM concentrations formed during each of the four-hour bulk decay tests on post-GAC waters are shown in Figure 6.34. Similar profiles, albeit of different magnitude, were observed at each of the WTWs, with a characteristic rapid initial formation followed by a declining rate. Between 27 and 39 % of the TTHM formed in the four-hour test period occurred within the initial five-minute period. In parallel with chlorine decay, the paths of

THM formation over the four-hour period were similar for the two different sampling weeks at each of the WTWs, except at Melbourne WTW and Draycote WTW.

The relationship between chlorine consumed and THM formed at several time intervals through these four-hour test periods was plotted (with the data not constrained through the origin in Figures 6.35 and 6.36, and with the data constrained through the origin in Figures 6.37 and 6.38). R^2 values for the unconstrained correlation of data ranged from 0.83 to 0.99 (significant at the 1 % level, average ~ 0.95, s.d. ~ 0.05). Each of the y-intercepts showed a close proximity to the origin (average ~ ± 2.09 µg/l, s.d. ~ 1.69 µg/l). Constraining the lines through the origin to satisfy the conditions for a constant K_{TC} value, did not lead to a significant change in the gradients of the lines, with an overall mean change of ± 2.69 µg/l THM per mg/l Cl (s.d. ~ 1.91), suggesting this process to be fit for purpose.

The speciation of THM in each of the tests varied through the four-hour test period, with an increasing propensity to form brominated species. The average BIF increased over the first hour, suggesting the rate of bromine incorporation increased due to the competing reaction kinetics of HOBr and HOCl, but then for the remainder of the test period displayed a plateau (Figure 6.39). Plots of bromide consumed versus TTHM formed show the parameters to be relatively proportionate over the four-hour time period (Figures 6.40 and 6.41), mirroring the relationship between chlorine consumed and TTHM formed (WTW sampling weeks where credible bromide data was not available or, suggested an increase in bromide concentration with time, were intentionally omitted from these plots).

TTHM formed and chlorine consumed over the two-hour variation tests on WTW post-GAC waters were used to calculate K_{TC} values (summarized in Table 6.3). These data were collated using stepwise regression to assemble predictive equations for determining K_{TC} values in relation to C_0, TOC, bromide and temperature of the form shown in equation 6.3. The coefficients for each of the six WTW are displayed in Table 6.2. The predicted K_{TC} values versus the observed K_{TC} values for each of the six WTWs are collectively displayed in Figure 6.42. The data is skewed around the 45 °C line with higher K_{TC} values generally being under-predicted and lower K_{TC} values being over-predicted. This is possibly due to the curve fitting process averaging out the random fluctuations. The K_{TC} value equations were used in conjunction with the equivalent WTW chlorine predictive equations from section 5.8 to determine TTHM concentrations after two-hours using the same method described in section 6.6.3. Summaries of the results are shown in Figure 6.43, with good overall fit across the six WTW combined. The average difference in predicted concentrations compared to observed concentrations across the six WTWs is ± 3.4 µg/l (or ± 11.8 %).

The relationship between the amounts of chlorine consumed across the contact tank in comparison to the final water TTHM concentrations are displayed in Figures 6.44 to 6.48. As with Strensham WTW, this does not account directly for the chlorine that would have been consumed, and THM formed, between the contact tank outlet and the final water sampling points. The accuracy is further limited by the sampling errors detailed earlier. However, taking into consideration these inaccuracies, the plots do provide an approximation to the relative reactivity of the different waters, and provide a useful basis for comparison of productivity between the WTWs given by the gradient of the trend lines shown (with the assumption that sampling errors, etc. are approximately the same across each of the six WTWs).

Of the six WTWs, Whitacre water can be seen to be the most productive in terms of THM formation, with a steeper gradient than the other WTWs, even though in general TOC and bromide concentrations were comparatively low. This is in agreement with results observed from the sampling day tests (Table 6.4). This is likely to be a result of the WTW having some of the highest chlorine concentrations at the contact tank inlet and large amounts of chlorine consumption across the contact tank, demonstrating the potential reactivity of this water even with low surrogate parameter concentrations. Whitacre WTW also had high THM concentrations at the final water consistently through the year in comparison to other WTW, where seasonal variations were more apparent (Figure 4.54).

Melbourne WTW (39.9), Strensham WTW (37.8) and Church Wilne WTW (37.2) each have similar gradients. Melbourne WTW and Church Wilne WTW exhibited relatively low contact tank inlet free chlorine concentrations in comparison to Strensham WTW, but each of the three WTWs saw similar amounts of chlorine consumed by the contact tank outlet.

In general, Draycote WTW had higher contact tank inlet free chlorine concentrations and relatively large amounts of chlorine consumed in comparison to Melbourne WTW and Church Wilne WTW. THM concentrations are similar, but due to the large amounts of chlorine typically consumed the gradient (21.0) is lower at Draycote WTW.

Campion Hills WTW displayed average inlet free chlorine concentrations relative to the other WTWs. However, due to it having the lowest chlorine consumption across the contact tank, and also the lowest amount of THM formed by the end of the treatment stream, the gradient (18.0) was the lowest. Across the final water service reservoir (also shown in Figure 6.48), the gradient of the line is not significantly lower than that observed across the WTW, showing the water to be productive in its early stages of the distribution system. The long retention time across the service reservoir (approximately 24 hours) leads to the final water THM concentrations being high in comparison to the other WTWs (Figure 4.54). An average of 17.2 µg/l TTHM is formed across this service reservoir, accounting for approximately half of the final water THM concentration.

Comparison of final water reactivity is difficult due to the differences in ambient conditions between WTWs and between sampling days. TTHM concentrations formed over the 24-hour test period are shown in Figure 6.49. Whitacre WTW, again produces large increases in THM concentrations (average of 22 µg/l), along with Campion Hills WTW (24.5 µg/l) and Draycote WTW (25.5 µg/l). Although Campion Hills WTW was seen not to have significant THM formation in the post-GAC tests, significant formation occurred in the final water tests (post-FWSR).

Differences between THM concentrations formed in final water and final DSR bulk decay tests over 24-hours (Figure 6.50) show an approximate 50 % decline in the amount of THM formed in the final water test to the amount formed at the DSR outlet towards the end of most of the distribution systems, with magnitude in the differences being related to the variation of distribution system length described in Chapter 4. K_{TC} values were calculated for each of the tests, determined by the amount of TTHM formed and chlorine consumed over the 24 hour test period. The results are shown in Table 6.3. Similar to the results at Strensham WTW, the values reflect the large variability attributed to the differences in ambient test conditions and water quality. Average K_{TC} values at the final waters were 84.1 µg/l TTHM per mg/l free Cl (s.d. ~ 20.6) rising to an average of 97.3 µg/l TTHM per mg/l free Cl (s.d. ~ 29.4) in the distribution system tests.

6.9 Conclusions

- Laboratory data showed successive treatment processes at Strensham WTW to remove cumulative amounts of THM precursor material, resulting in a decline in TTHM formation during two-hour tests conducted on water through the WTW at similar test conditions (Figure 6.1). The average TTHM concentration formed fell from 33.3 µg/l average at raw water to 18.3 µg/l at the post-GAC sampling point. The greatest reduction occurred across the clarification process (where a 6.8 µg/l difference was observed between average raw and post-clarifier samples).

- A propensity to remove organic matter with little change in bromide led to a shift from chloroform as the predominant THM species at the inlet of the Strensham WTW (78 %) to an increase in the percentage share of brominated species (with chloroform only accounted for 38 % of TTHM by post-GAC samples). Corresponding BIFs also reflected this, increasing from 0.28 at the raw water to 1.10 at the post-GAC stage.

- Mirroring the decay of chlorine, the rate of THM formation was initially rapid, followed by a declining rate (approximately 43 % of the total amount of THM formed over two-hours occurs within the initial five-minutes of the start of the test) (Figures 6.12 and 6.13).

- Bromide conversion was also greatest in the early stages of these tests, with 36 % (21.1 µg/l) and 51 % (22.8 µg/l) drops in the initial bromide concentrations on the 1st and 2nd sampling weeks half way through the 4-hour tests.

- THM formation was shown to increase with contact time, C_0, temperature, TOC, and bromide concentrations. Bromide was positively, and TOC negatively, linked with a higher fraction of chloroform as a percentage of TTHM species and lower BIF (Figure 6.15). The decline in bromide conversion over the 2-hour bulk decay tests was greater with higher C_0 and temperatures.

- THM formation at Strensham WTW was found to be higher in the summer months than spring months for similar TOC and bromide concentrations in the water, indicating a different, potentially more reactive chemical matrix of the water in the summer months; a concern when considering other seasonal factors such as temperature being higher in the summer months.

- The use of K_{TC} values (the amount of unit THM produced per unit chlorine consumed) was shown to be an expedient basis for estimating THM formation in operational circumstances.

- All post-GAC water tests at Strensham WTW suggested an average K_{TC} value across the contact tank to be 39 µg/l TTHM per mg/l free Cl. With the omission of sample water dilution tests, which showed unpredictably high THM concentrations, this average dropped to 34 µg/l TTHM per mg/l free Cl.

- All the data from post-GAC tests was collated using SPSS (via stepwise regression) to develop an equation for calculating K_{TC} values of the form:

$$K_{TC} = A + (a \cdot C_0) + (b \cdot \Theta) + (c \cdot TOC) + (d \cdot Br) \qquad (6.3)$$

- This equation was used in combination with the chlorine modelling equations developed in Chapter 5 to calculate THM concentrations after two-hours for each of the different test conditions. In general, THM concentrations were slightly over-predicted, although the predicted concentrations were usually within ± 5 µg/l TTHM (average of ± 3.9 µg/l, or 13.8 %) of the observed concentrations (for Stensham WTW tests alone); and ± 5 µg/l TTHM (average of ± 3.4 µg/l, or 11.8 %) of the observed concentrations across the six WTWs.

- K_{TC} values were shown not to have a statistical dependence on temperature, there was a weak dependence on chlorine, TOC and bromide (to a level of 15 % significance*).* A probable explanation for this is the complicated effect of varying bromide : chlorine, bromide : TOC, and chlorine : TOC ratios.

Sampling location	Date	Test conditions				Calculation of K_{tc} value (µg/l / mg/l free Cl)			
		C_0 (mg/l)	TOC (mg/l)	Temperature (°C)	Bromide (µg/l)	Time (hrs)	Free Cl consumed (mg/l)	TTHM produced (µg/l)	K_{tc} value (µg/l / mg/l free Cl)
Raw water	04.06.07	1.7	4.8	15	66.1	2	1.63	34.9	21.4
	30.07.07	1.7	8.2	15	56.5	2	1.66	46.2	27.8
	05.02.08	1.7	4.1	15	72.5	2	1.70	23.1	13.6
	11.02.08	1.7	3.9	15	59.8	2	1.61	34.1	21.2
	21.02.08	1.7	3.1	15	97.8	2	1.66	30.1	18.2
	26.02.08	1.7	2.8	15	94.8	2	1.60	35.5	22.2
	04.03.08	1.7	5.9	15	44.1	2	1.70	40.0	23.5
	18.03.08	1.7	1.5	15	45.9	2	1.70	28.0	16.5
	21.04.08	1.7	4.1	15	39.6	2	1.65	27.8	16.9
	Average	**1.7**	**4.2**	**15**	**64.1**	**2**	**1.68**	**33.3**	**20.1**
Post-clarifier	05.02.08	1.7	2.8	15	-	2	1.11	30.1	27.2
	11.02.08	1.7	2.8	15	-	2	0.92	21.2	23.0
	21.02.08	1.7	2.2	15	-	2	1.08	26.8	24.8
	26.02.08	1.7	1.8	15	-	2	0.99	27.3	27.6
	04.03.08	1.7	2.4	15	-	2	1.05	29.5	28.2
	18.03.08	1.7	1.5	15	-	2	1.03	20.2	19.6
	21.04.08	1.7	3.2	15	-	2	1.34	30.0	22.4
	Average	**1.7**	**2.4**	**15**	**-**	**2**	**1.07**	**26.5**	**24.7**
Post-RGF	05.02.08	1.7	2.4	15	-	2	0.91	20.2	22.4
	11.02.08	1.7	2.3	15	-	2	0.80	21.4	26.8
	21.02.08	1.7	2.2	15	-	2	0.86	23.8	27.7
	26.02.08	1.7	1.8	15	-	2	0.88	25.1	28.7
	04.03.08	1.7	2.0	15	-	2	0.81	25.5	31.4
	18.03.08	1.7	1.3	15	-	2	0.82	20.7	25.2
	21.04.08	1.7	2.9	15	-	2	1.09	28.2	26.0

Sampling location	**Date**	**Test conditions**				**Calculation of K_{tc} value (µg/l / mg/l free Cl)**			
		C_0 (mg/l)	**TOC (mg/l)**	**Temperature (°C)**	**Bromide (µg/l)**	**Time (hrs)**	**Free Cl consumed (mg/l)**	**TTHM produced (µg/l)**	**K_{tc} value (µg/l / mg/l free Cl)**
	Average	**1.7**	**2.1**	**15**	**-**	**2**	**0.88**	**23.6**	**26.9**
Post-GAC	01.03.07	0.34	2.1	15	-	2	0.30	8.4	28.0
	27.03.07	0.41	2.5	15	-	2	0.31	8.5	27.4
	27.03.07	1.9	2.5	15	-	2	0.64	14.6	22.8
	04.06.07	1.7	2.3	15	58.3	2	0.77	27.4	35.6
	04.06.07	1.7	2.3	5	58.3	2	0.53	20.9	39.4
	04.06.07	1.7	2.3	25	58.3	2	0.81	31.8	39.3
	04.06.07	1.7	0.8 (1:2)	15	19.4 (1:2)	2	0.25	22.7	90.8
	04.06.07	1.7	1.6 (2:1)	15	38.9 (2:1)	2	0.37	26.2	70.8
	04.06.07	1.3	2.3	15	58.3	2	0.48	26.0	54.2
	04.06.07	2.1	2.3	15	58.3	2	0.74	29.3	39.6
	04.06.07	1.8	2.3	17	58.3	2	0.73	28.6	39.2
	30.07.07	1.7	3.0	15	44.3	2	0.68	26.5	39.0
	30.07.07	1.7	3.0	5	44.3	2	0.59	23.0	39.0
	30.07.07	1.7	3.0	25	44.3	2	0.92	36.3	39.5
	30.07.07	1.7	1.0 (1:2)	15	14.7 (1:2)	2	0.31	22.8	73.5
	30.07.07	1.7	2.0 (2:1)	15	29.5 (2:1)	2	0.59	22.1	37.5
	30.07.07	1.3	3.0	15	44.3	2	0.64	22.2	34.7
	30.07.07	2.1	3.0	15	44.3	2	0.72	28.4	39.4
	30.07.07	1.9	3.0	16	44.3	2	0.86	25.4	29.5
	05.02.08	1.7	1.9	15	13.8	2	0.65	14.8	22.8
	11.02.08	1.7	2.0	15	56.4	2	0.48	12.2	25.4
	21.02.08	1.7	1.7	15	95.4	2	0.56	17.8	32.1
	26.02.08	1.7	1.7	15	90.8	2	0.50	17.5	35.0
	04.03.08	1.7	1.7	15	45.1	2	0.53	18.0	34.3

Sampling location	Date	Test conditions				Calculation of K_{tc} value (µg/l / mg/l free Cl)			
		C_0 (mg/l)	TOC (mg/l)	Temperature (°C)	Bromide (µg/l)	Time (hrs)	Free Cl consumed (mg/l)	TTHM produced (µg/l)	K_{tc} value (µg/l / mg/l free Cl)
	18.03.08	1.7	1.3	15	41.4	2	0.51	14.0	27.7
	21.04.08	1.7	2.4	15	33.2	2	0.71	16.6	23.4
	Average	**1.6**	**2.3**	**15**	**52.2**	**2**	**0.58**	**21.6**	**39.2**
Final water	02.08.06	0.5	2.1	21.5	-	24	0.34	22.9	67.4
	01.03.07	0.34	2.1	8.8	-	24	0.23	10.3	44.8
	27.03.07	0.41	1.8	10.1	-	24	0.24	10.5	43.8
	04.06.07	0.32	2.3	17.0	42.7	24	0.23	21.1	91.7
	30.07.07	0.36	2.9	17.2	<12	24	0.26	17.6	67.7
	05.02.08	0.47	2.0	6.5	9.1	24	0.22	8.4	38.2
	11.02.08	0.34	1.9	7.0	34.6	24	0.20	12.5	62.5
	21.02.08	0.40	1.7	4.1	64.8	24	0.17	5.5	32.4
	26.02.08	0.39	1.7	7.5	61.7	24	0.24	8.9	37.1
	04.03.08	0.45	1.8	7.0	25.6	24	0.26	8.9	34.2
	18.03.08	0.42	1.3	8.0	27.8	24	0.26	13.8	53.1
	21.04.08	0.47	2.3	8.6	23.4	24	0.31	9.7	31.3
	Average	**0.41**	**2.0**	**10.3**	**36.2**	**24**	**0.25**	**12.5**	**50.4**
Oversley Green BPS outlet	02.08.06	0.21	-	20.8	-	24	0.13	10.5	80.9
	04.06.07	0.32	-	16.5	-	24	0.20	15.2	76.0
	30.07.07	0.34	-	17.0	-	24	0.22	13.4	61.0
	05.02.08	0.37	-	6.9	-	24	0.14	7.4	52.9
	11.02.08	0.25	-	7.1	-	24	0.12	7.3	60.8
	21.02.08	0.36	-	4.3	-	24	0.12	4.4	36.6
	26.02.08	0.32	-	7.5	-	24	0.13	9.4	72.3
	04.03.08	0.29	-	7.1	-	24	0.14	6.4	45.4
	18.03.08	0.32	-	7.2	-	24	0.16	11.1	69.4

Sampling location	**Date**	**Test conditions**				**Calculation of K_{tc} value (µg/l / mg/l free Cl)**			
		C_0 (mg/l)	**TOC (mg/l)**	**Temperature (°C)**	**Bromide (µg/l)**	**Time (hrs)**	**Free Cl consumed (mg/l)**	**TTHM produced (µg/l)**	**K_{tc} value (µg/l / mg/l free Cl)**
	21.04.08	0.34	-	8.9	-	24	0.19	7.4	38.7
	Average	**0.31**	**-**	**10.3**	**-**	**24**	**0.16**	**9.3**	**59.4**
Tysoe DSR outlet	04.06.07	0.13	-	16.5	-	24	0.07	6.9	99.7
	30.07.07	0.10	-	17.6	-	24	0.06	10.9	180.8
	11.02.08	0.21	-	6.9	-	24	0.08	5.0	62.5
	21.02.08	0.22	-	4.5	-	24	0.06	6.8	113.3
	26.02.08	0.23	-	7.2	-	24	0.08	6.2	77.5
	04.03.08	0.22	-	6.8	-	24	0.07	6.4	91.4
	21.04.08	0.11	-	8.6	-	24	0.05	4.9	98.8
	Average	**0.17**	**-**	**9.7**	**-**	**24**	**0.07**	**6.7**	**103.4**

Table 6.1; Calculation of K_{tc} values for bulk decay tests through Strensham WTW and Shipston distribution system on all sampling days.

	Coefficients for equations of the form; $K_{TC} = A + (a \cdot C_0) + (b \cdot \Theta) + (c \cdot TOC) + (d \cdot Br)$				
Parameter	**Constant**	**Initial Cl (C_0)**	**Temperature (Θ)**	**TOC**	**Br**
Coefficient	**A**	**a**	**b**	**c**	**d**
WTW					
Strensham WTW	26.6029	-10.2772	0.0275	6.9109	0.1828
Whitacre WTW	129.813	-7.6565	0.0258	-22.269	0.1622
Melbourne WTW	98.4500	-3.3175	-0.0034	-25.683	0.4180
Draycote WTW	92.71	-0.093	0.142	-18.573	?
Church Wilne WTW	107.642	-9.086	0.207	-29.362	?
Campion Hills WTW	130.2283	0.7464	-0.5075	-20.4478	-0.2725

Table 6.2; Coefficients for the predictive equations at individual WTWs to predict K_{TC} values (question marks indicate absence of bromide in predictive equation due to lack of bromide data or sampling errors).

Sampling location / WTW		**Date**	**Test conditions**				**Calculation of K_{TC} value (µg/l / mg/l free Cl)**			
			C_0 (mg/l)	**TOC (mg/l)**	**Temperature (°C)**	**Bromide (µg/l)**	**Time (hrs)**	**Free Cl consumed (mg/l)**	**TTHM produced (µg/l)**	**K_{tc} value (µg/l / mg/l free Cl)**
Raw water	**Draycote WTW**	21.06.06	1.7	6.5	18.7	121.0	2	1.63	71.3	43.7
		31.07.06	1.7	7.0	22.1	91.7	2	1.68	68.7	40.9
		11.07.07	1.7	6.2	15.0	81.7	2	1.56	64.5	41.3
		20.08.07	1.7	6.4	15.0	89.2	2	1.63	42.9	26.3
		Average	**1.7**	**6.5**	**17.7**	**95.9**	**2**	**1.63**	**61.9**	**38.1**
	Campion Hills WTW	03.08.06	1.7	6.8	15.0	100	2	1.65	68.4	41.4
		11.06.07	1.7	5.3	15.0	88.4	2	1.66	49.9	49.9
		13.08.07	1.7	5.8	15.0	<12	2	1.65	54.8	54.8
		Average	**1.7**	**6.0**	**15.0**	**94.2**	**2**	**1.65**	**57.7**	**48.7**
	Church Wilne WTW	24.09.07	1.7	3.1	15.0	37.5	2	1.63	56.9	34.9
		01.10.07	1.7	3.1	15.0	102.3	2	1.69	70.7	41.8
		Average	**1.7**	**3.1**	**15.0**	**69.9**	**2**	**166**	**63.8**	**38.4**
	Melbourne WTW	16.07.07	1.7	4.0	15.0	57.9	2	1.62	68.0	42.0
		08.10.07	1.7	4.4	15.0	52.3	2	1.45	52.1	36.0
		Average	**1.7**	**4.2**	**15.0**	**55.1**	**2**	**1.54**	**60.1**	**39.0**
	Whitacre WTW	06.08.07	1.7	7.4	15.0	113.2	2	1.54	64.2	41.7
		10.09.07	1.7	5.5	15.0	105.6	2	1.64	54.4	33.2
		Average	**1.7**	**6.5**	**15.0**	**109.4**	**2**	**1.69**	**59.3**	**37.5**
Post-GAC water	**Draycote WTW**	20.08.07	1.7	3.5	15.0	<12	2	0.74	22.1	29.9
		20.08.07	1.7	3.5	5.0	<12	2	0.50	14.3	28.6
		20.08.07	1.7	3.5	25.0	<12	2	0.86	26.9	31.3
		20.08.07	1.7	1.2 (1:2)	15.0	<12	2	0.27	21.4	79.3
		20.08.07	1.7	2.4 (2:1)	15.0	<12	2	0.55	21.1	38.4
		20.08.07	1.3	3.5	15.0	<12	2	0.66	20.4	30.9

Sampling location / WTW	**Date**	**Test conditions**				**Calculation of K_{TC} value (µg/l / mg/l free Cl)**			
		C_0 (mg/l)	**TOC (mg/l)**	**Temperature (°C)**	**Bromide (µg/l)**	**Time (hrs)**	**Free Cl consumed (mg/l)**	**TTHM produced (µg/l)**	**K_{tc} value (µg/l / mg/l free Cl)**
	20.08.07	2.1	3.5	15.0	<12	2	0.79	24.2	30.6
	20.08.07	1.8	3.5	18.6	<12	2	0.76	23.6	31.1
	Average	**1.7**	**3.1**	**15.5**	**<12**	**2**	**0.64**	**21.8**	**37.5 (31.4)**
Campion Hills WTW	11.06.07	1.7	2.7	15.0	78.2	2	0.58	29.1	50.2
	11.06.07	1.7	2.7	5.0	78.2	2	0.38	23.1	60.8
	11.06.07	1.7	2.7	25.0	78.2	2	0.80	38.8	48.5
	11.06.07	1.7	0.9 (1:2)	15.0	26.1 (1:2)	2	0.28	28.7	102.5
	11.06.07	1.7	1.8 (2:1)	15.0	52.1 (2:1)	2	0.48	27.9	58.1
	11.06.07	1.3	2.7	15.0	78.2	2	0.49	26.4	53.9
	11.06.07	2.1	2.7	15.0	78.2	2	0.66	32.7	49.5
	11.06.07	1.6	2.7	17.7	78.2	2	0.86	23.4	27.2
	Average	**1.7**	**2.4**	**15.3**	**68.4**	**2**	**0.57**	**28.8**	**56.3 (49.5)**
Campion Hills WTW	13.08.07	1.7	3.3	15.0	60.6	2	0.62	24.9	40.2
	13.08.07	1.7	3.3	5.0	60.6	2	0.48	19.7	41.0
	13.08.07	1.7	3.3	25.0	60.6	2	0.83	30.6	36.9
	13.08.07	1.7	1.1 (1:2)	15.0	20.2 (1:2)	2	0.26	26.5	101.9
	13.08.07	1.7	2.2 (2:1)	15.0	40.4 (2:1)	2	0.46	28.4	61.7
	13.08.07	1.3	3.3	15.0	60.6	2	0.55	23.2	42.2
	13.08.07	2.1	3.3	15.0	60.6	2	0.66	27.0	40.9
	13.08.07	1.9	3.3	18.4	60.6	2	0.66	25.5	38.6
	Average	**1.7**	**2.9**	**15.4**	**53.0**	**2**	**0.57**	**25.7**	**50.4 (41.5)**

Sampling location / WTW	**Date**	**Test conditions**				**Calculation of K_{TC} value (µg/l / mg/l free Cl)**			
		C_0 (mg/l)	**TOC (mg/l)**	**Temperature (°C)**	**Bromide (µg/l)**	**Time (hrs)**	**Free Cl consumed (mg/l)**	**TTHM produced (µg/l)**	**K_{tc} value (µg/l / mg/l free Cl)**
Church Wilne WTW	24.09.07	1.7	1.9	15.0	<12	2	0.57	27.7	41.9
	24.09.07	1.7	1.9	5.0	<12	2	0.61	24.5	40.2
	24.09.07	1.7	1.9	25.0	<12	2	0.81	38.6	47.7
	24.09.07	1.7	0.6 (1:2)	15.0	<12	2	0.33	27.0	81.8
	24.09.07	1.7	1.2 (2:1)	15.0	<12	2	0.54	25.7	48.0
	24.09.07	1.3	1.9	15.0	<12	2	0.54	24.9	46.1
	24.09.07	2.1	1.9	15.0	<12	2	0.69	29.8	34.7
	24.09.07	1.6	1.9	18.0	<12	2	0.65	23.3	35.8
	Average	**1.7**	**1.7**	**15.4**	**<12**	**2**	**0.59**	**27.7**	**47.0 (41.9)**
Church Wilne WTW	01.10.07	1.7	1.8	15.0	97.3	2	0.72	29.7	41.3
	01.10.07	1.7	1.8	5.0	97.3	2	0.58	26.5	46.1
	01.10.07	1.7	1.8	25.0	97.3	2	0.80	38.6	48.3
	01.10.07	1.7	0.6 (1:2)	15.0	32.4 (1:2)	2	0.27	22.2	82.2
	01.10.07	1.7	1.2 (2:1)	15.0	64.8 (2:1)	2	0.52	25.8	50.1
	01.10.07	1.3	1.8	15.0	97.3	2	0.64	26.9	42.4
	01.10.07	2.1	1.8	15.0	97.3	2	0.81	32.7	36.7
	01.10.07	1.6	1.8	15.5	97.3	2	0.72	28.6	39.7
	Average	**1.7**	**1.6**	**15.1**	**85.1**	**2**	**0.63**	**28.9**	**48.4 (43.3)**
Melbourne WTW	16.07.07	1.7	2.8	15.0	63.0	2	0.84	35.7	42.5
	16.07.07	1.7	2.8	5.0	63.0	2	0.67	32.2	48.4
	16.07.07	1.7	2.8	25.0	63.0	2	0.97	46.0	47.7
	16.07.07	1.7	0.9 (1:2)	15.0	21.0 (1:2)	2	0.28	27.5	100.0

Sampling location / WTW	Date	Test conditions				Calculation of K_{TC} value (μg/l / mg/l free Cl)			
		C_0 (mg/l)	TOC (mg/l)	Temperature (°C)	Bromide (μg/l)	Time (hrs)	Free Cl consumed (mg/l)	TTHM produced (μg/l)	K_{tc} value (μg/l / mg/l free Cl)
	16.07.07	1.7	1.9 (2:1)	15.0	42.0 (2:1)	2	0.53	34.9	65.8
	16.07.07	1.3	2.8	15.0	63.0	2	0.77	33.7	46.5
	16.07.07	2.1	2.8	15.0	63.0	2	0.88	38.0	43.4
	16.07.07	1.4	2.8	18.0	63.0	2	0.84	38.5	45.8
	Average	**1.7**	**2.5**	**15.4**	**55.1**	**2**	**0.72**	**35.8**	**55.0 (47.0)**
Melbourne WTW	08.10.07	1.7	3.0	15.0	49.1	2	0.61	25.7	42.1
	08.10.07	1.7	3.0	5.0	49.1	2	0.55	20.0	36.7
	08.10.07	1.7	3.0	25.0	49.1	2	0.89	34.1	38.3
	08.10.07	1.7	1.0 (1:2)	15.0	16.4 (1:2)	2	0.35	19.3	55.1
	08.10.07	1.7	2.0 (2:1)	15.0	32.7 (2:1)	2	0.51	21.9	43.4
	08.10.07	1.3	3.0	15.0	49.1	2	0.58	24.8	42.8
	08.10.07	2.1	3.0	15.0	49.1	2	0.76	27.7	36.7
	08.10.07	1.6	3.0	16.7	49.1	2	0.77	23.3	30.3
	Average	**1.7**	**2.6**	**15.2**	**42.9**	**2**	**0.63**	**24.6**	**40.7 (38.2)**
Whitacre WTW	06.08.07	1.7	3.5	15.0	42.2	2	0.70	32.4	46.3
	06.08.07	1.7	3.5	5.0	42.2	2	0.57	27.9	48.9
	06.08.07	1.7	3.5	25.0	42.2	2	0.94	46.3	49.3
	06.08.07	1.7	1.2 (1:2)	15.0	14.1 (1:2)	2	0.25	27.4	109.6
	06.08.07	1.7	2.4 (2:1)	15.0	28.1 (2:1)	2	0.53	32.3	60.9
	06.08.07	1.3	3.5	15.0	42.2	2	0.70	33.0	47.1
	06.08.07	2.1	3.5	15.0	42.2	2	0.84	34.0	40.5
	06.08.07	2.0	3.5	17.0	42.2	2	0.87	38.4	44.1

Sampling location / WTW		**Date**	**Test conditions**				**Calculation of K_{TC} value (µg/l / mg/l free Cl)**			
			C_0 (mg/l)	**TOC (mg/l)**	**Temperature (°C)**	**Bromide (µg/l)**	**Time (hrs)**	**Free Cl consumed (mg/l)**	**TTHM produced (µg/l)**	**K_{tc} value (µg/l / mg/l free Cl)**
		Average	**1.7**	**3.1**	**15.3**	**36.9**	**2**	**0.68**	**33.9**	**55.8 (47.4)**
	Whitacre WTW	10.09.07	1.7	3.4	15.0	19.2	2	0.83	39.4	47.5
		10.09.07	1.7	3.4	5.0	19.2	2	0.64	29.8	46.6
		10.09.07	1.7	3.4	25.0	19.2	2	1.02	48.4	47.5
		10.09.07	1.7	1.1(1:2)	15.0	6.4 (1:2)	2	0.34	29.5	86.8
		10.09.07	1.7	2.3 (2:1)	15.0	12.8 (2:1)	2	0.61	36.2	59.3
		10.09.07	1.3	3.4	15.0	19.2	2	0.72	36.5	50.7
		10.09.07	2.1	3.4	15.0	19.2	2	0.85	39.1	46.0
		10.09.07	1.9	3.4	17.0	19.2	2	0.91	38.3	42.1
		Average	**1.7**	**2.9**	**15.3**	**16.8**	**2**	**0.74**	**37.2**	**53.3 (47.6)**
WTW final water	**Draycote WTW**	**21.06.06**	0.42	4.1	18.7	49.2	24	0.27	24.8	91.9
		31.07.06	0.46	4.8	22.1	40.9	24	0.30	27.9	92.8
		11.07.07	0.43	3.6	17.8	<12	24	0.22	22.0	100.0
		20.08.07	0.50	4.0	18.6	46.1	24	0.28	26.9	96.1
		Average	**0.45**	**4.1**	**19.3**	**45.4**	**24**	**0.27**	**25.4**	**95.2**
	Campion Hills WTW	03.08.06	0.48	2.6	18.6	45.3	24	0.25	26.8	107.0
		11.06.07	0.45	2.6	18.0	31.4	24	0.22	24.6	111.8
		13.08.07	0.42	3.1	18.5	<12	24	0.20	22.2	110.8
		Average	**0.45**	**2.8**	**18.4**	**38.4**	**24**	**0.22**	**24.5**	**109.9**
	Church Wilne WTW	24.09.07	0.51	1.7	19.5	49.8	24	0.34	16.7	49.1
		01.10.07	0.55	1.7	15.5	23.3	24	0.22	16.3	58.2
		Average	**0.53**	**1.7**	**17.5**	**26.6**	**24**	**0.28**	**12.9**	**53.7**

Sampling location / WTW		Date	Test conditions				Calculation of K_{TC} value (µg/l / mg/l free Cl)			
			C_0 (mg/l)	TOC (mg/l)	Temperature (°C)	Bromide (µg/l)	Time (hrs)	Free Cl consumed (mg/l)	TTHM produced (µg/l)	K_{tc} value (µg/l / mg/l free Cl)
	Melbourne WTW	16.07.07	0.43	2.7	16.7	30.4	24	0.29	17.3	59.7
		08.10.07	0.47	3.0	14.9	21.7	24	0.26	21.5	82.7
		Average	**0.45**	**2.9**	**15.8**	**26.1**	**24**	**0.28**	**19.4**	**71.2**
	Whitacre WTW	06.08.07	0.53	2.9	17.4	24.7	24	0.32	24.8	77.4
		10.09.07	0.50	2.8	17.1	<12	24	0.27	19.2	71.1
		Average	**0.52**	**2.9**	**17.3**	**24.7**	**24**	**0.30**	**22**	**74.3**
Draycote D.S.	**Flecknoe DSR**	11.07.07	0.16	-	17.8	-	24	0.06	5.1	85.7
	Napton DSR	20.08.07	0.15	-	18.6	-	24	0.07	8.1	116.3
		Average	**0.16**	**-**	**18.2**	**-**	**24**	**0.07**	**6.6**	**101**
Campion Hills D.S.	**Priors Marston DSR**	11.06.07	0.23	-	18.0	-	24	0.08	10.2	127.4
	Priors Marston DSR	13.08.07	0.37	-	18.5	-	24	0.14	11.4	81.6
		Average	**0.30**	**-**	**18.3**	**-**	**24**	**0.11**	**10.8**	**104.5**
Church Wilne D.S	**Bramcote DSR**	01.10.07	0.18	-	15.1	-	24	0.10	16.2	161.7

Sampling location / WTW		Date	Test conditions				Calculation of K_{TC} value (µg/l / mg/l free Cl)			
			C_0 (mg/l)	TOC (mg/l)	Temperature (°C)	Bromide (µg/l)	Time (hrs)	Free Cl consumed (mg/l)	TTHM produced (µg/l)	K_{tc} value (µg/l / mg/l free Cl)
Whitacre D.S	**Tuttle Hill DSR**	06.08.07	0.14	-	17.3	-	24	0.08	6.2	78.0
	Tuttle Hill DSR	10.09.07	0.26	-	17.1	-	24	0.10	7.8	78.2
		Average	**0.20**	**-**	**17.2**	**-**	**24**	**0.09**	**7.0**	**78.1**
Melbourne D.S.	**Oadby DSR No.2**	16.07.07	0.41	-	16.2	-	24	0.11	6.23	56.6

Table 6.3; Summary of THM results and the calculation of K_{TC} values for bulk decay tests through Draycote, Campion Hills, Church Wilne, Melbourne and Whitace WTWs and associated distribution systems on all sampling days.

WTW	**Sample Week**	**Spot sample taken through WTWs**					**Averages of all tests on post-GAC waters (bracketed values without sample water dilution tests)**			**C.T free Cl + F.W TTHM on same sampling days (averages) (Oct. 2006 – Oct. 2008)**
		Pre-contact tank	**Post-contact tank**			**Final water**				
		Free Cl (mg/l)	*Free Cl (mg/l)*	*TTHM (µg/l)*	K_{TC} *value (µg/l TTHM / mg/l Cl)*	*TTHM (µg/l)*	*Free Cl consumed (mg/l)*	*TTHM (µg/l)*	K_{TC} *value (µg/l TTHM / mg/l Cl)*	K_{TC} *value (µg/l TTHM / mg/l Cl)*
Whitacre WTW	1	2.10	1.42	35.1	51.6	41.0	0.68	33.9	55.8 (47.4)	69.0
	2	1.90	1.61	29.0	100.0	35.0	0.74	37.2	53.3 (47.6)	
Melbourne WTW	1	1.43	0.99	23.1	52.5	38.8	0.72	35.8	55.0 (47.0)	39.9
	2	1.58	1.12	15.5	33.7	20.0	0.63	24.6	40.7 (38.2)	
Draycote WTW	1	1.64	1.22	25.5	60.7	26.1	-	-	-	21.0
	2	1.71	1.29	23.0	54.8	24.9	0.64	21.8	37.5 (31.4)	
Campion Hills WTW	1	1.54	1.14	15.4	38.5	39.9	0.57	28.8	56.3 (49.5)	18.0
	2	1.66	1.24	17.0	40.5	36.2	0.57	25.7	50.4 (41.5)	
Church Wilne WTW	1	1.34	1.02	23.2	72.5	21.8	0.59	27.7	47.0 (41.9)	37.1
	2	1.53	1.02	26.0	50.9	23.7	0.63	28.9	48.4 (43.3)	
Strensham WTW	1	1.92	1.56	23.7	65.8	31.1	0.59	26.6	51.1 (41.2)	37.7
	2	2.07	1.42	29.7	45.7	35.5	0.66	25.8	41.5 (36.9)	

Table 6.4; Summary of TTHM formation at each of the six WTWs on the summer 2007 sampling days at each of the 6 WTWs.

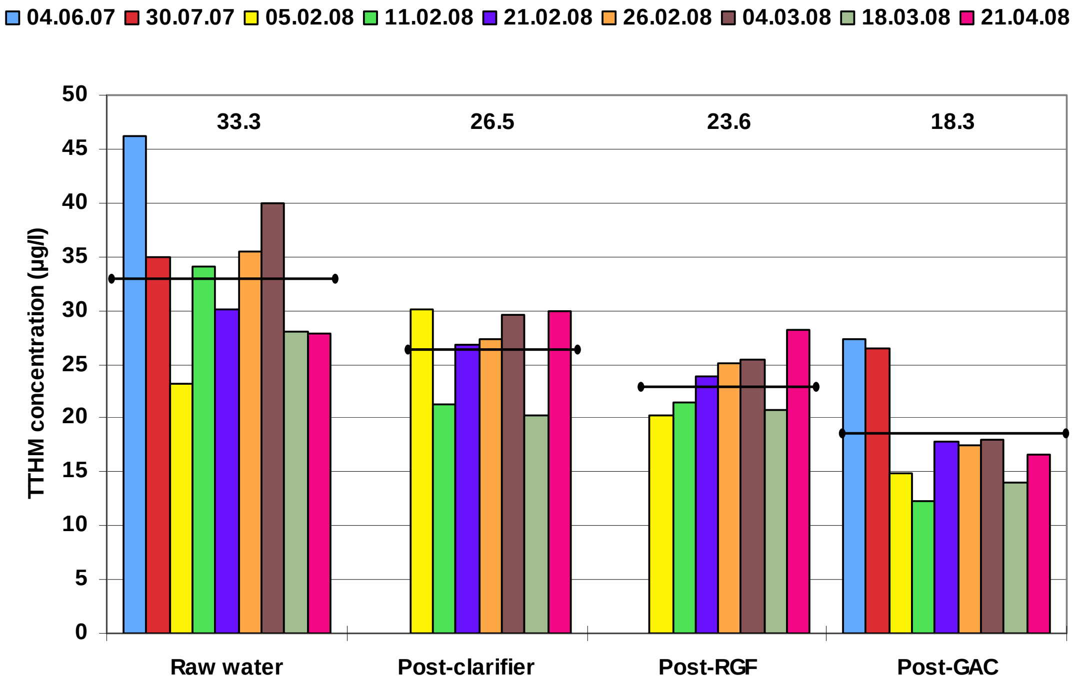


Figure 6.1; TTHM concentrations formed after 2-hour bulk decay tests on water sampled through Strensham WTW on different sampling days. All tests performed at 15°C, at ambient TOC, bromide concentrations and a C_0 (dosed) of 1.7 mg/l.

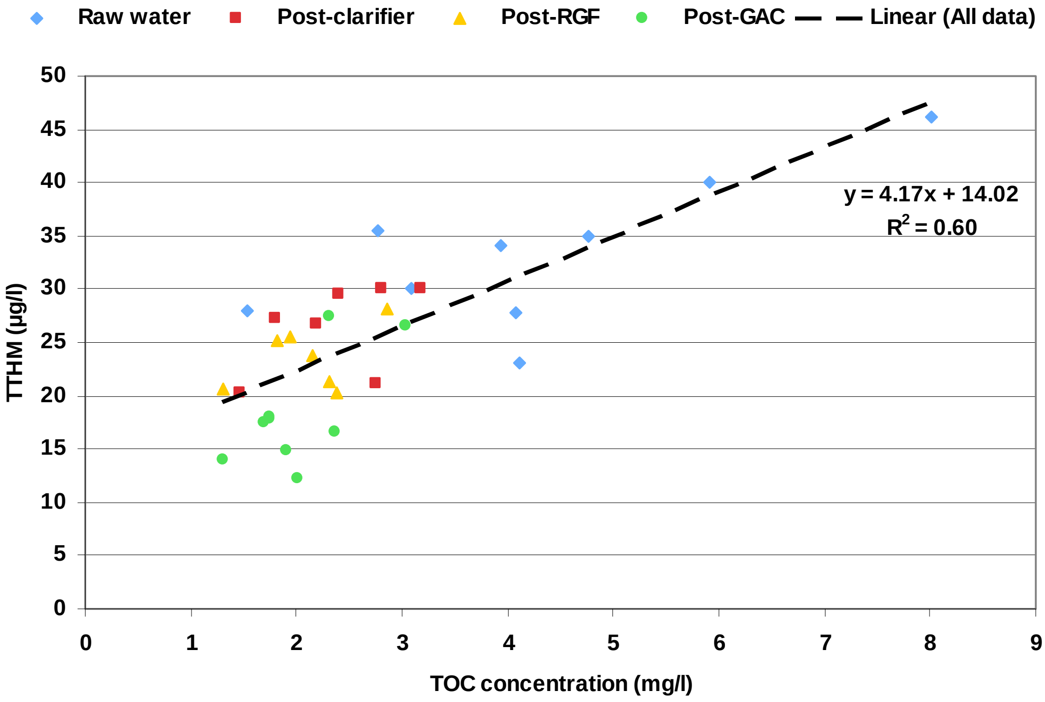


Figure 6.2; TTHM concentrations formed after 2-hour bulk decay tests on water sampled through Strensham WTW on different sampling days versus concurrent TOC spot samples at the sampling location (TTHM data depicted in Figure 6.1).

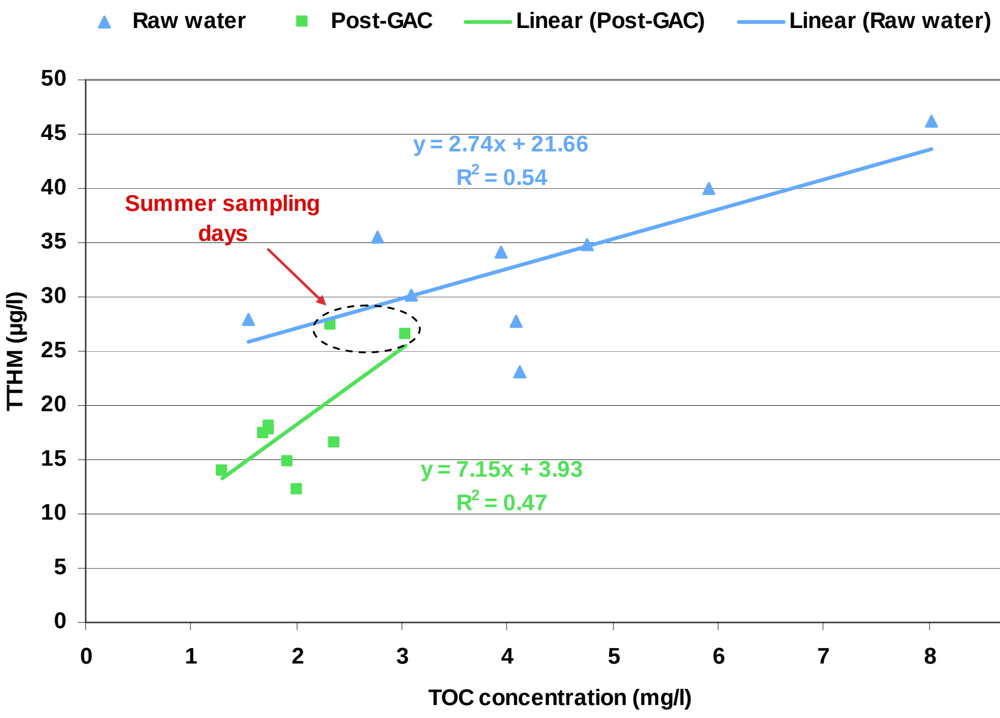


Figure 6.3; TTHM concentrations formed after 2-hour bulk decay tests on water sampled at raw and post-GAC sampling points at Strensham WTW on different sampling days versus concurrent TOC spot samples at the sampling location.

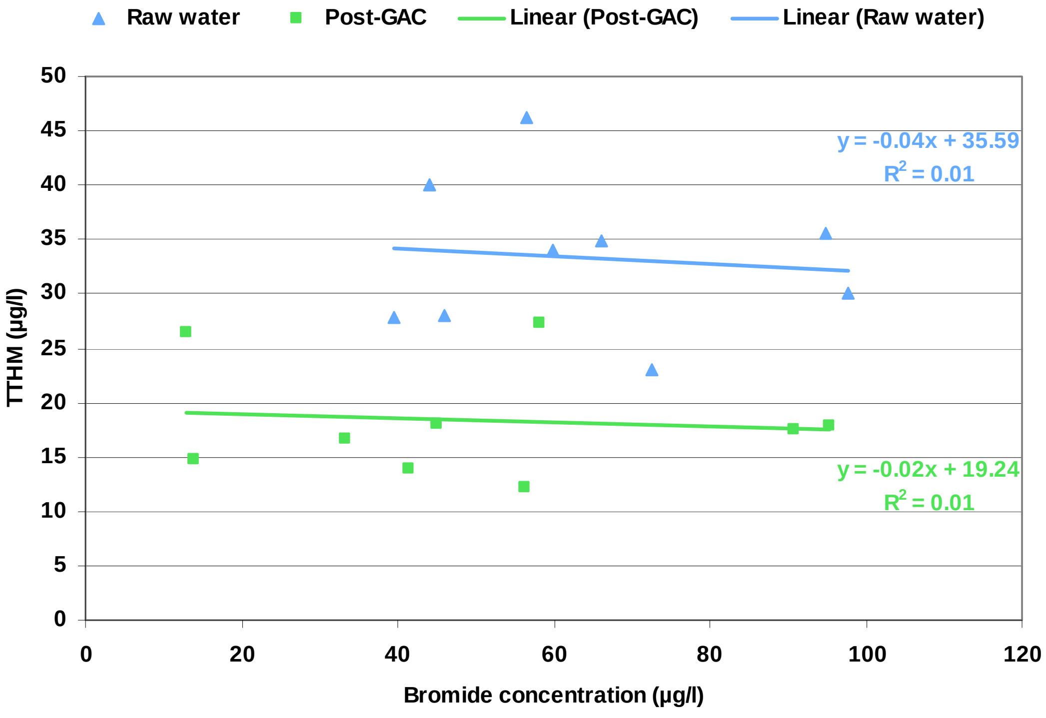


Figure 6.4; TTHM concentrations formed after 2-hour bulk decay tests on water sampled at raw and post-GAC sampling points at Strensham WTW on different sampling days versus concurrent bromide spot samples at the sampling location.

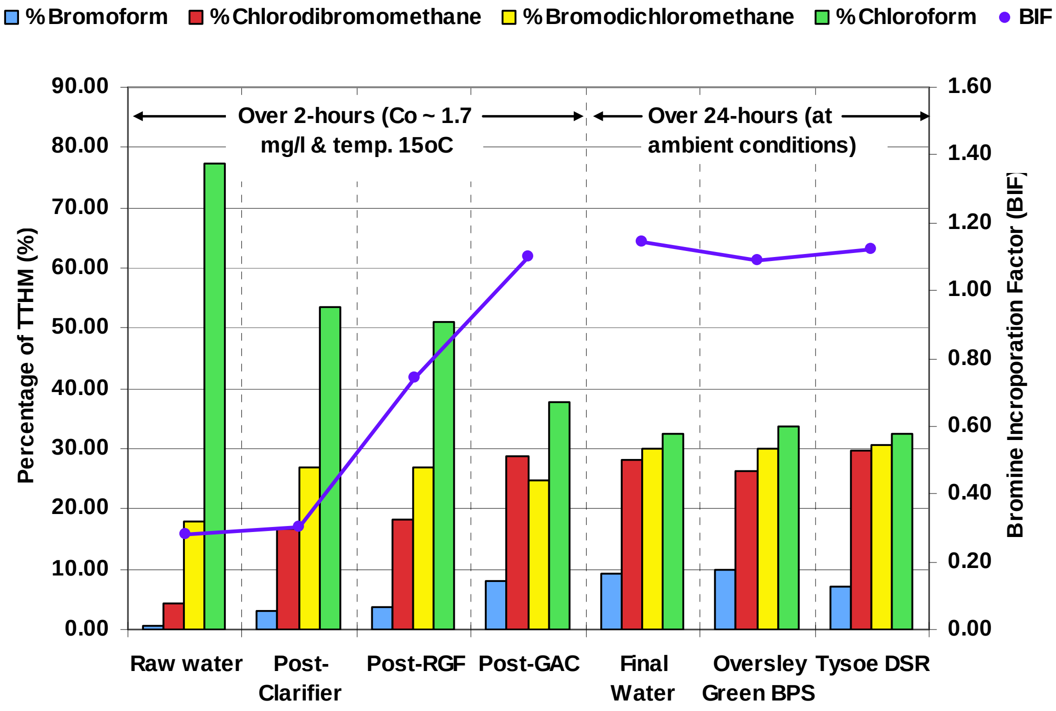


Figure 6.5; THM species as a percentage of TTHM and bromine incorporation factors. Based on averages of THM concentrations after 2-hour bulk decay tests through WTW and 24-hour bulk decay tests on final water and through distribution system.

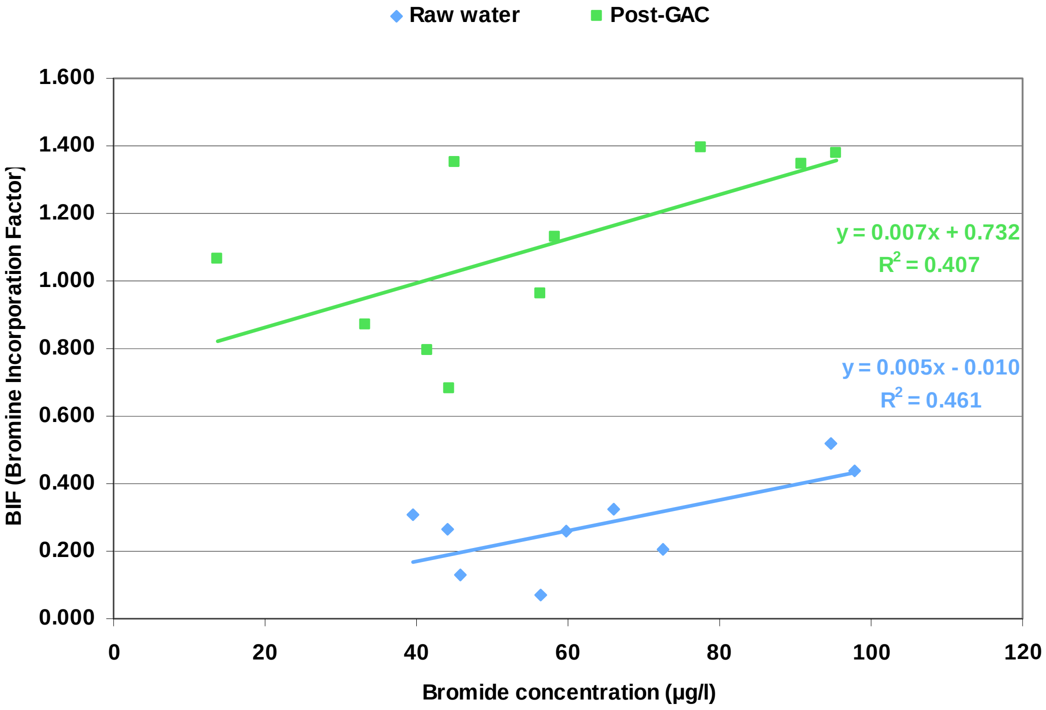


Figure 6.6; Bromide concentrations at the raw and post-GAC waters (at Strensham WTW) versus equivalent bromine incorporation factors (BIF) in THM measurements after 2-hour bulk decay tests.

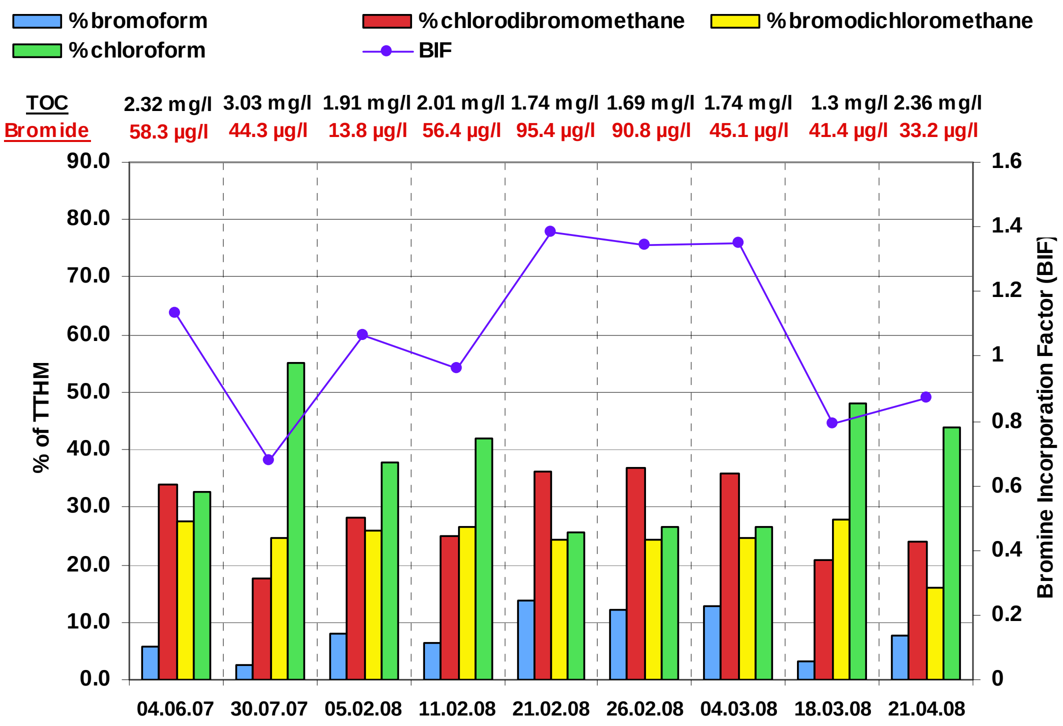


Figure 6.7; THM species as a percentage of TTHM after 2-hour bulk decay tests from sampling days at Strensham WTW on post-GAC waters conducted at an initial chlorine concentration of 1.7 mg/l and temperature of 15 ºC. Bromine incorporation factors on R.H.S y-axis.

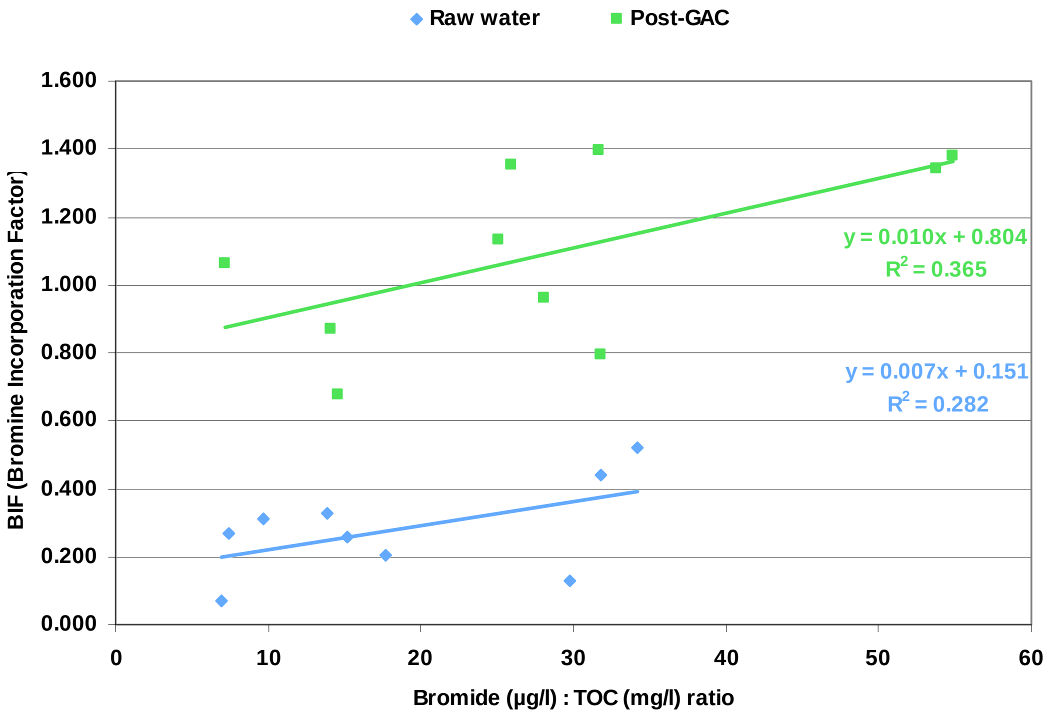


Figure 6.8 ; Bromide : TOC ratio at the raw and post-GAC waters (at Strensham WTW) versus equivalent bromine incorporation factors (BIF) in THM measurements after 2-hour bulk decay tests.

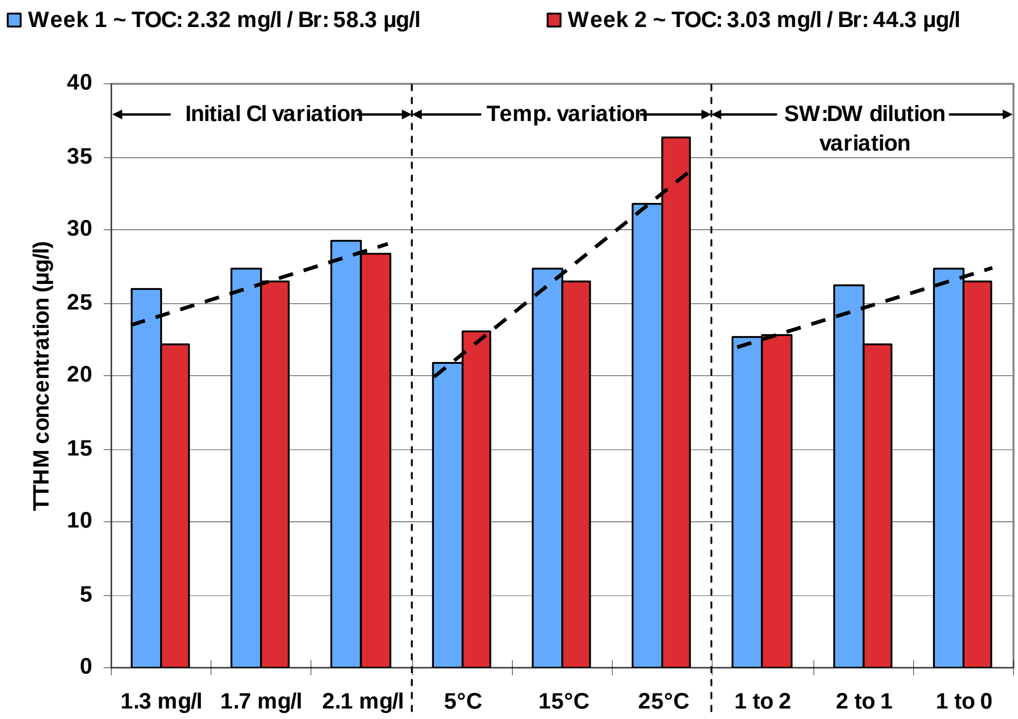


Figure 6.9; TTHM concentrations formed after 2-hour bulk decay tests with variations in initial chlorine concentration (1.3 / 1.7 / 2.1 mg/l), temperature (5 / 15 / 25 ^{o}C) and sample water : distilled water (SW:DW) dilution (1 to 2 / 2 to 1 / 1 to 0).

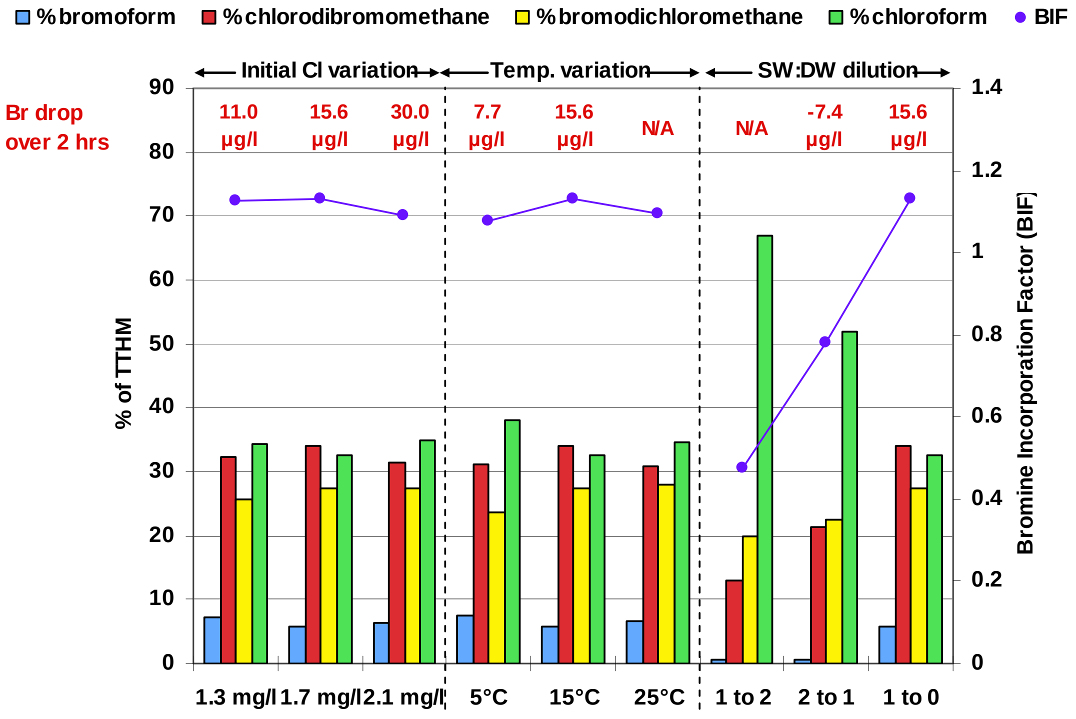


Figure 6.10; THM species as a percentage of TTHM and BIFs. From variation of bulk decay test conditions on post-GAC water at Strensham WTW on 04.06.07 sampling day. TOC and bromide concentration; 2.32 mg/l and 58.3 µg/l, respectively.

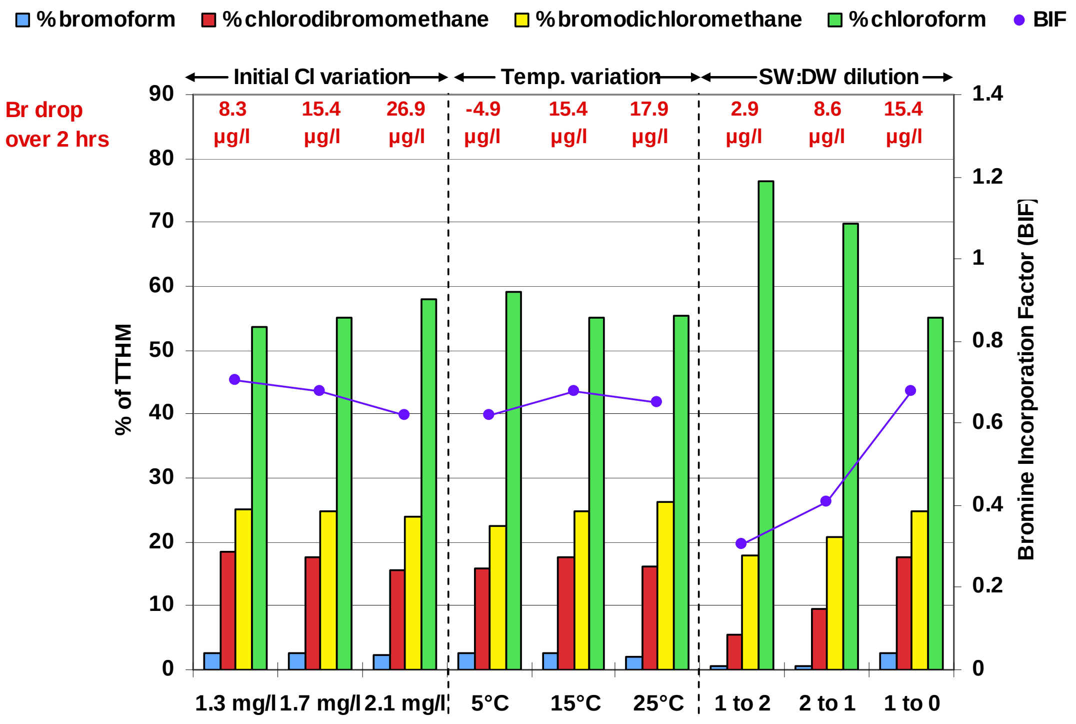


Figure 6.11; THM species as a percentage of TTHM and BIFs. From variation of bulk decay test conditions on post-GAC water at Strensham WTW on 30.07.07 sampling day. TOC and bromide concentration; 3.03 mg/l and 44.3 µg/l, respectively.

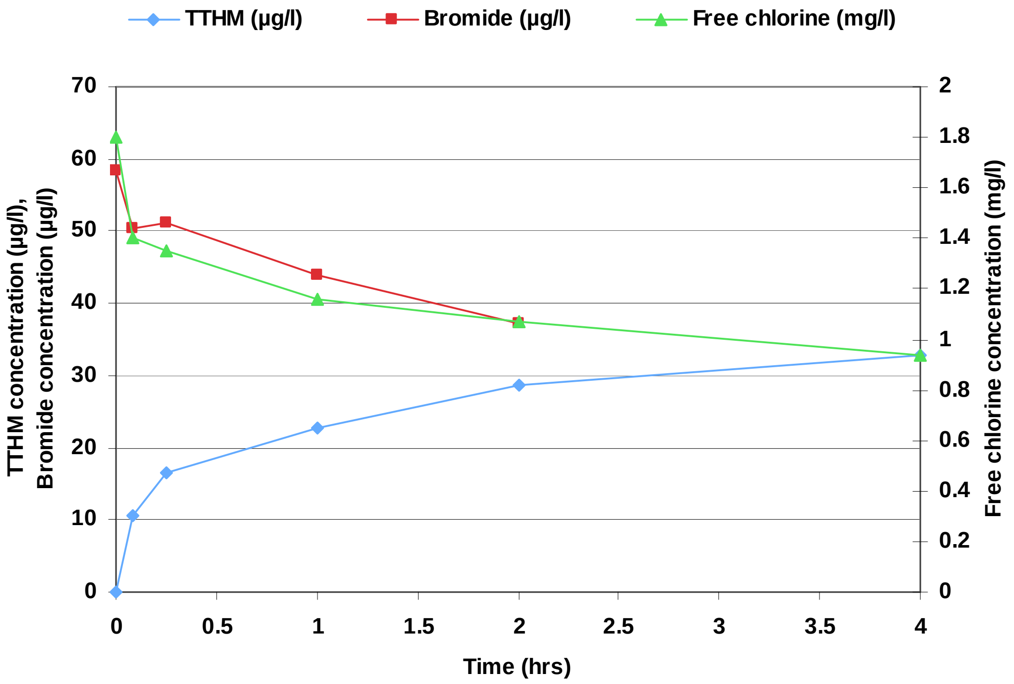


Figure 6.12; TTHM, bromide and free chlorine concentrations over the 4-hour bulk decay tests simulating ambient conditions across the contact tank on the day of sampling (04.06.07). Initial chlorine concentration 1.8 mg/l, temperature 17 °C, TOC concentration 2.32 mg/l and bromide concentration 58.3 µg/l.

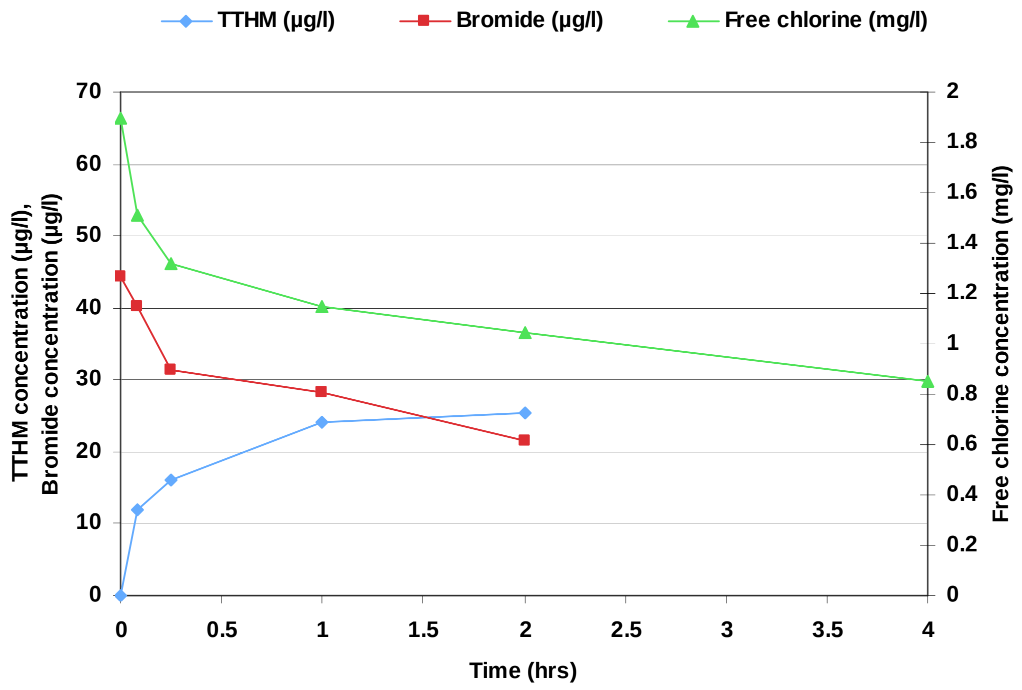


Figure 6.13; TTHM, bromide, and free chlorine concentrations over the 4-hour bulk decay tests simulating ambient conditions across the contact tank on the day of sampling (30.07.07). Initial chlorine concentration 1.9 mg/l, temperature 16 ºC, TOC concentration 3.03 mg/l, and bromide concentration 44.3 μg/l.

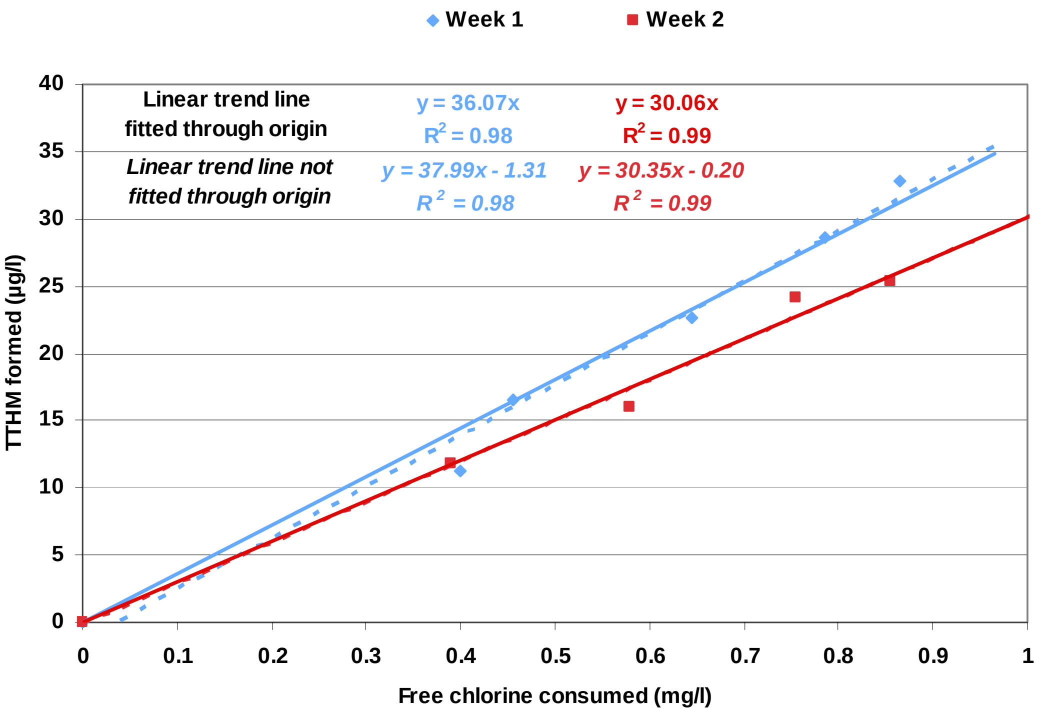


Figure 6.14; Free chlorine consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Strensham WTW. Dashed trend lines not fitted through origin.

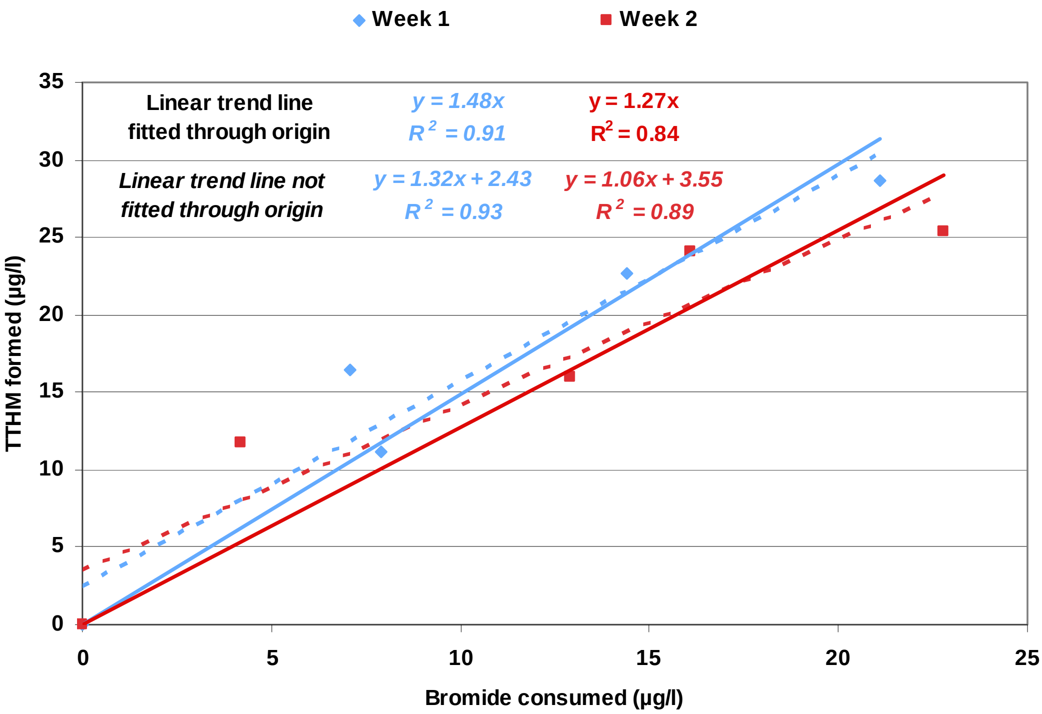


Figure 6.15 ; Bromide consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Strensham WTW. Dashed trend lines not fitted through origin.

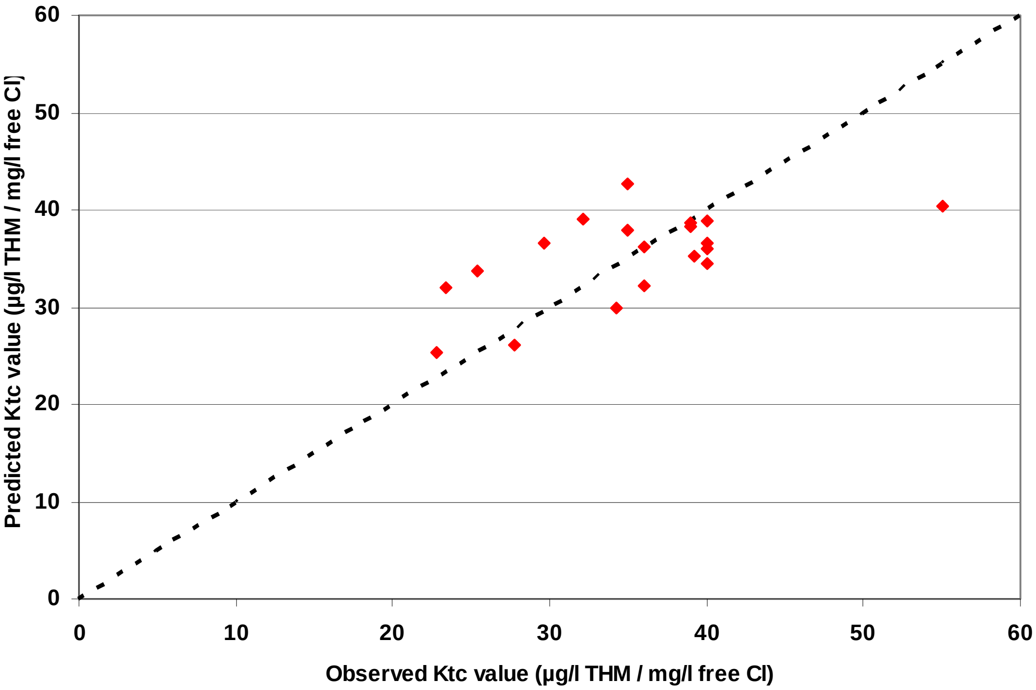


Figure 6.16; SPSS predicted vs. observed K_{TC} values for Strensham WTW, not including dilution data, but including all data (summer 07 and Spring 08).

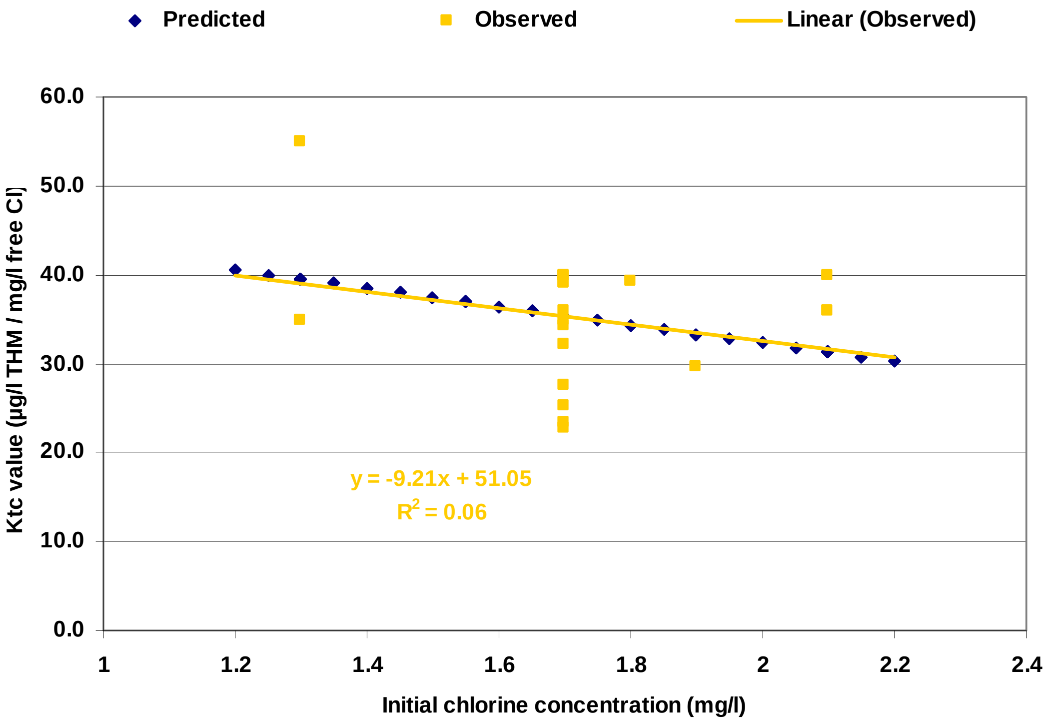


Figure 6.17; Predicted variation in the K_{TC} value with initial chlorine concentration (temperature, bromide and TOC concentrations held constant at mean values). Observed values from Strensham WTW in orange.

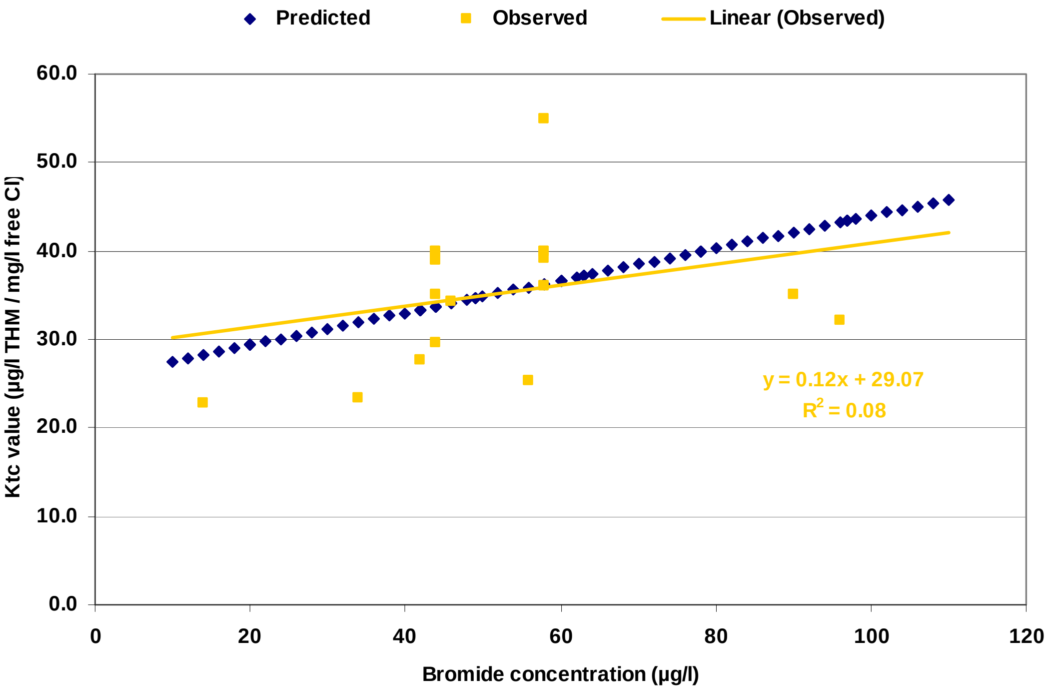


Figure 6.18; Predicted variation in the K_{TC} value with bromide concentration (temperature, C_0 and TOC concentrations held constant at mean values). Observed values from Strensham WTW in orange.

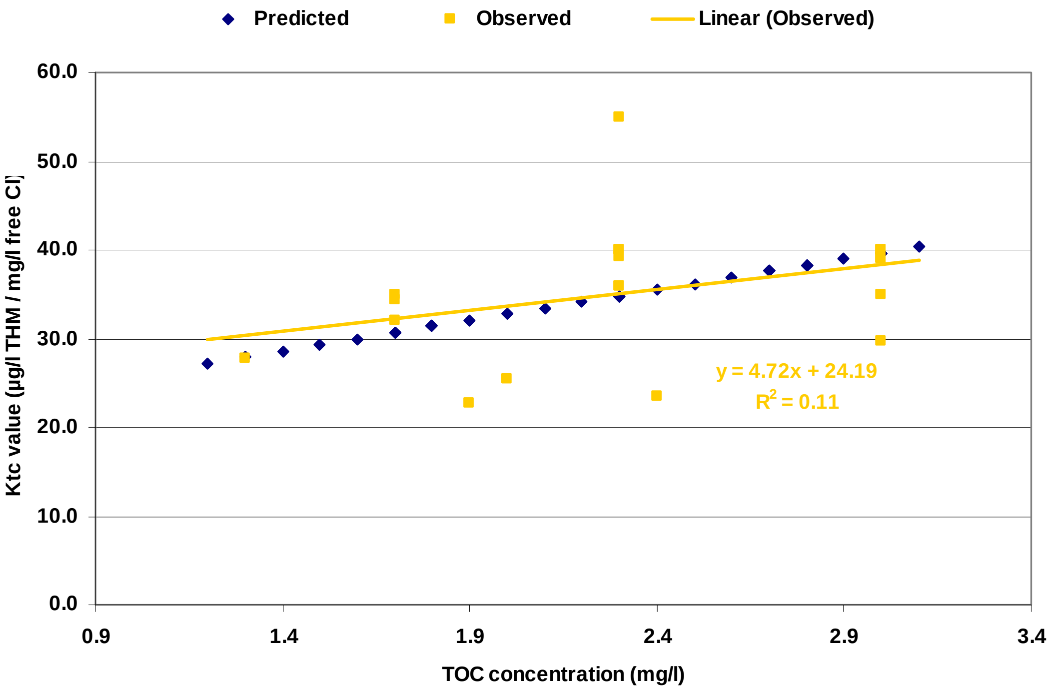


Figure 6.19; Predicted variation in the K_{TC} value with TOC concentration (temperature, C_0 and bromide concentrations held constant at mean values). Observed values from Strensham WTW in orange.

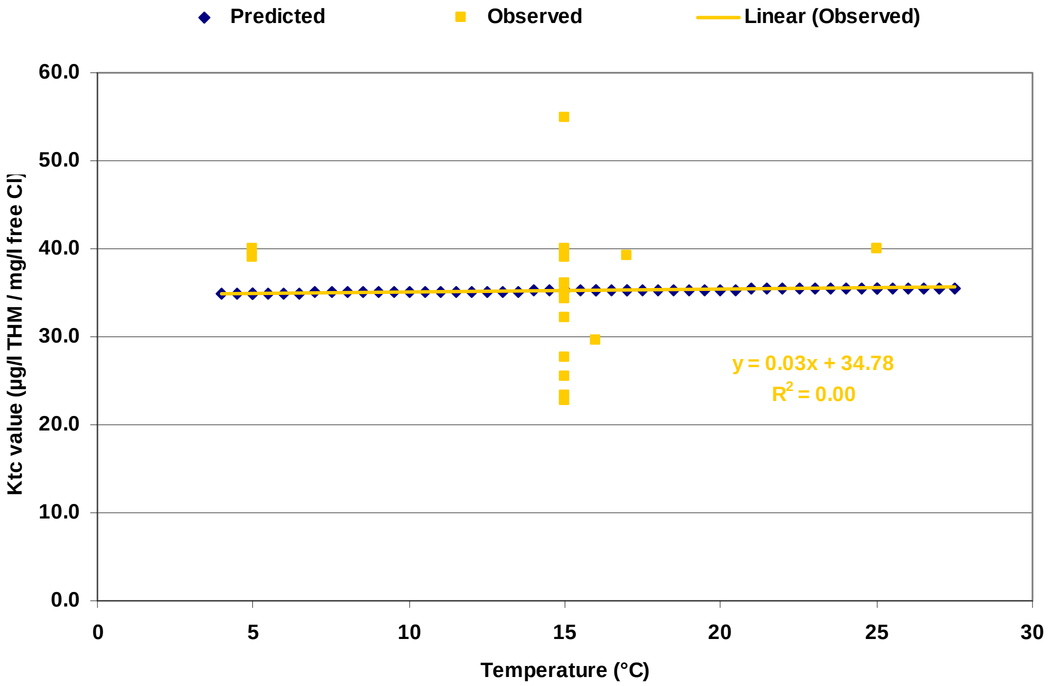


Figure 6.20; Predicted variation in the K_{TC} value with temperature (C_0, bromide and TOC concentrations held constant at mean values). Observed values from Strensham WTW in orange.

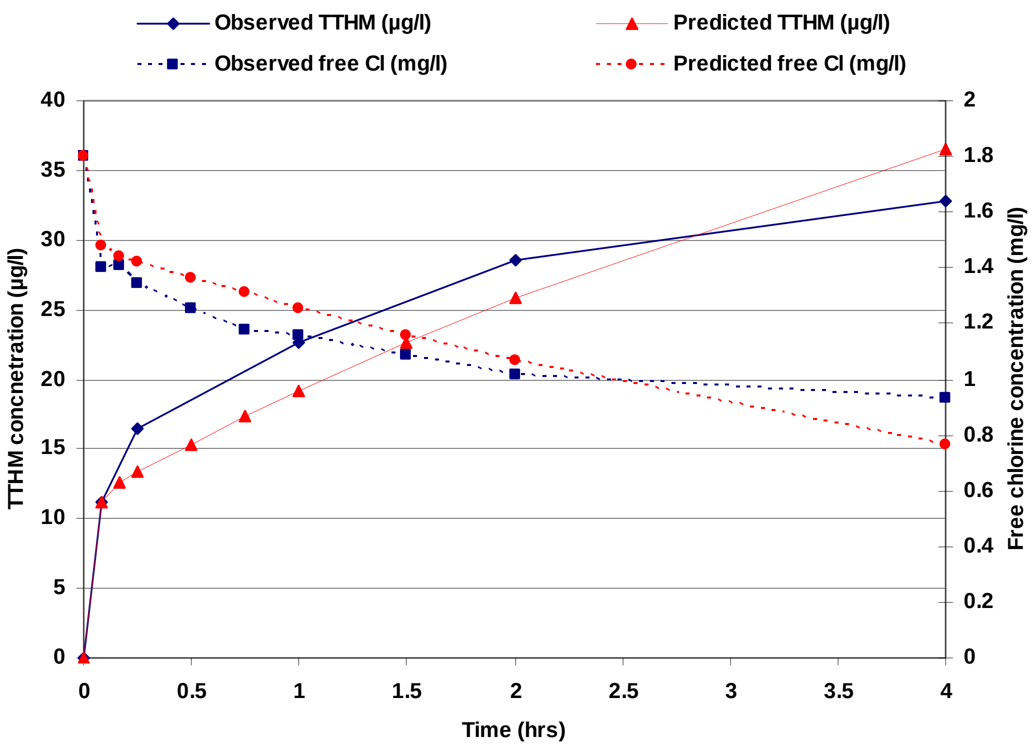


Figure 6.21; Observed and predicted free chlorine and TTHM concentrations over a 4-hour period (based on ambient conditions at post-GAC sampling point on 04.06.07).

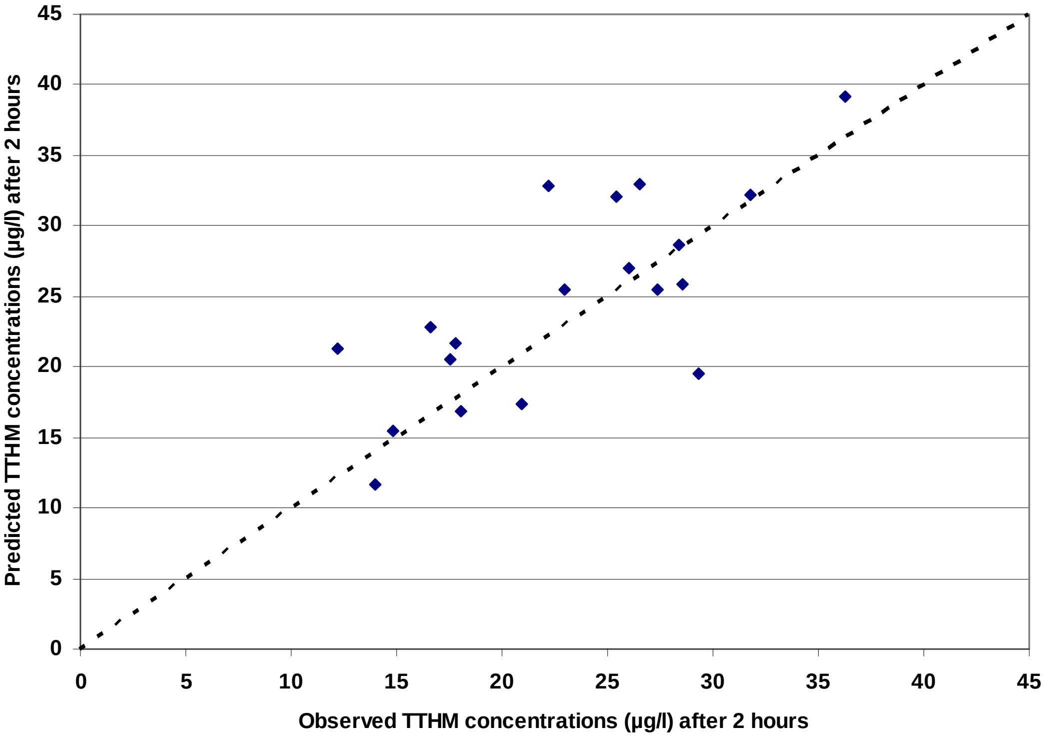


Figure 6.22; Observed versus predicted TTHM concentrations after 2-hours using predictive K_{TC} value equation in combination with the two stage chlorine decay modelling equations.

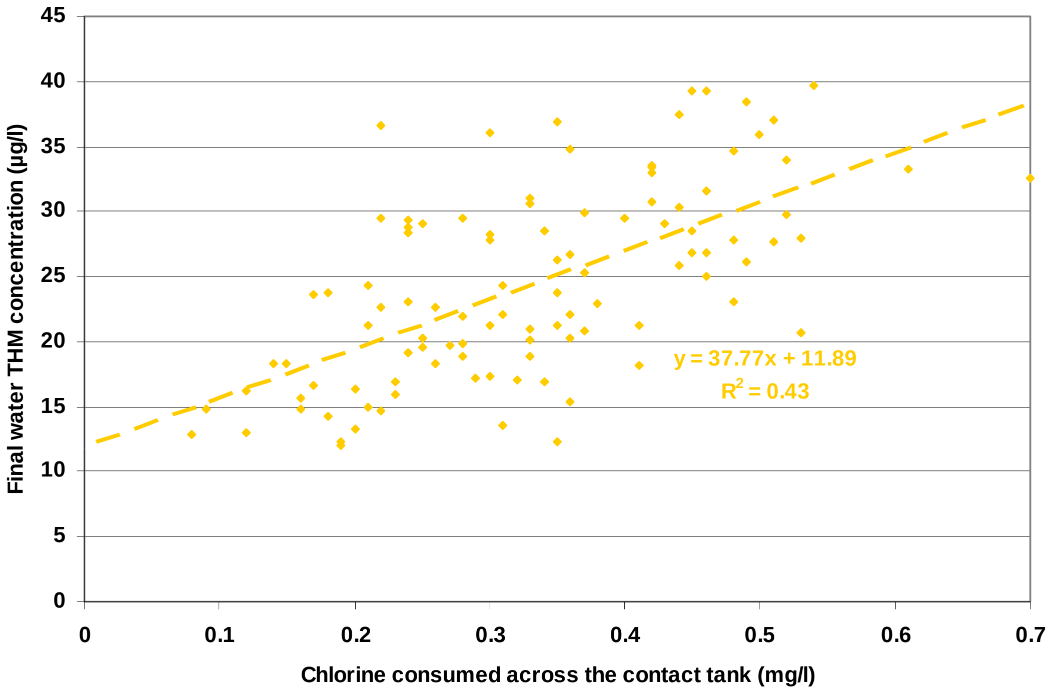


Figure 6.23; Final water THM concentrations vs. the decline in free chlorine concentrations between the pre- & post-contact tank sampling points on same days Based on STW data between October 2006 – October 2008 at Stensham WTW.

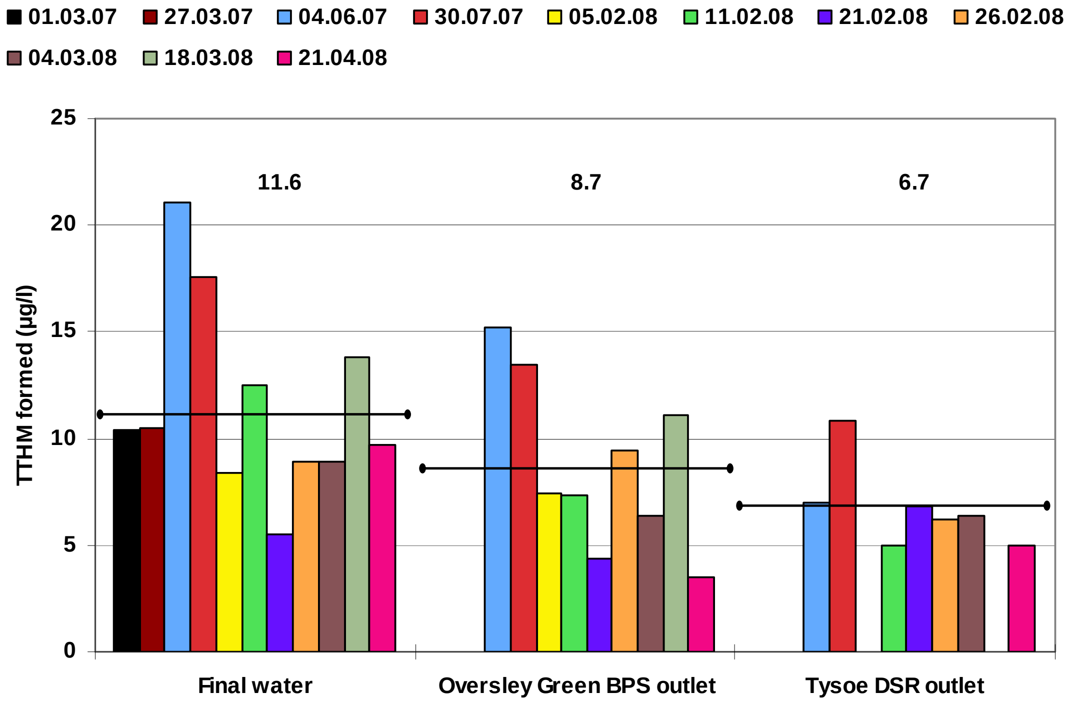


Figure 6.24; TTHM formed over 24-hour bulk decay tests on water from Strensham WTW final water, Oversley Green BPS outlet & Tysoe DSR outlet on different sampling days. All tests conducted at ambient chlorine, temperature and TOC concentrations.

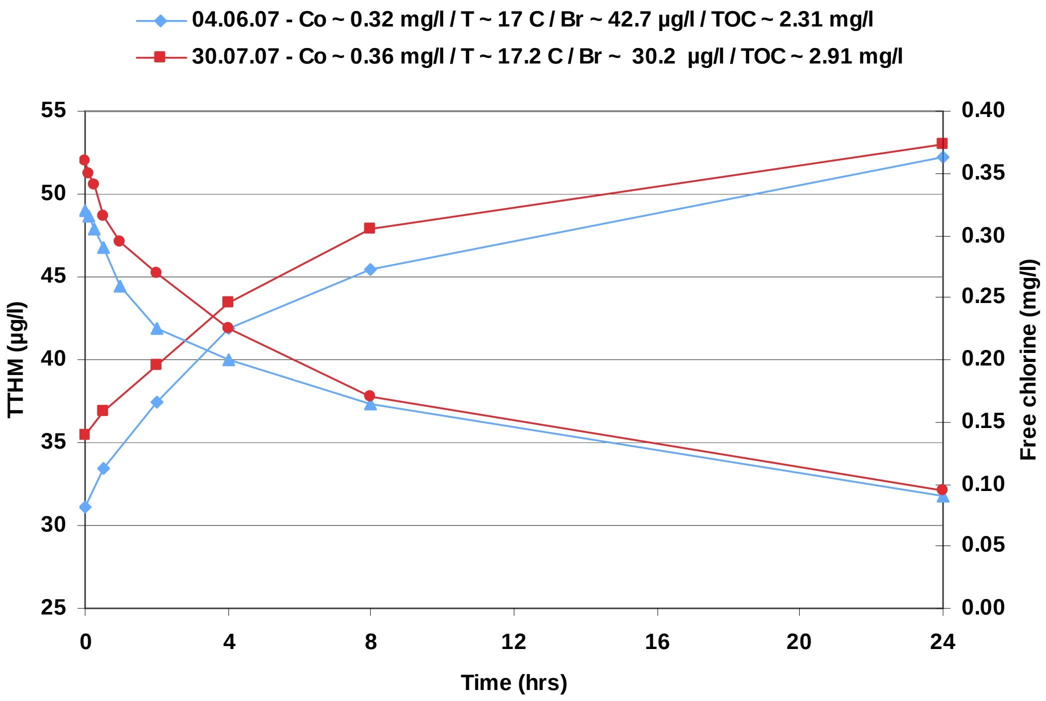


Figure 6.25; TTHM and free chlorine concentrations over the 24-hour bulk decay tests on Strensham WTW final water on the two summer 2007 sampling days.

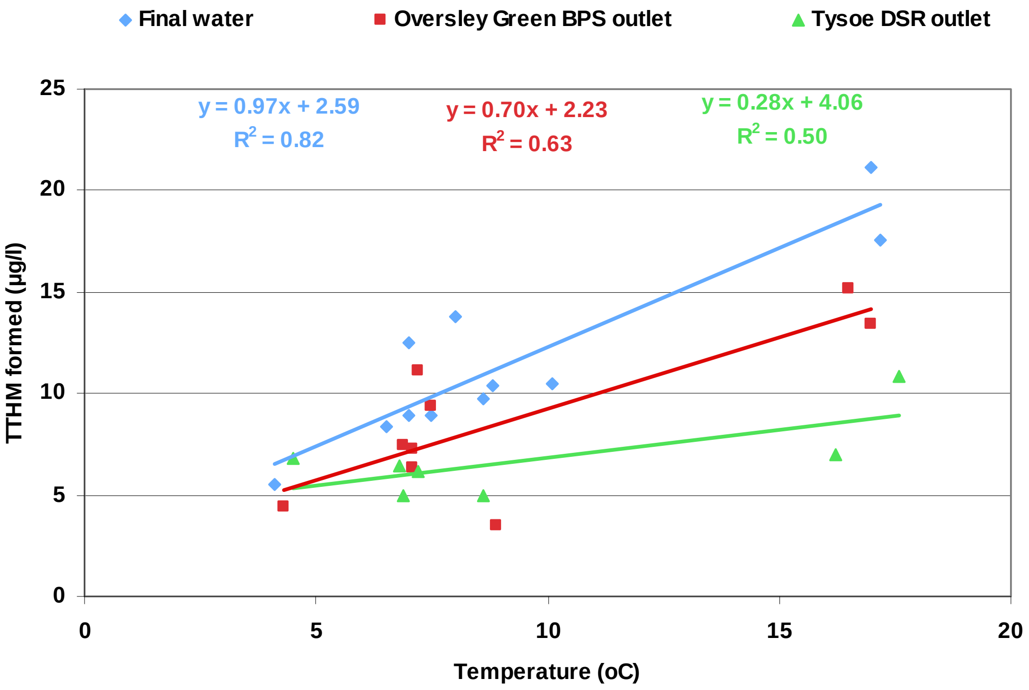


Figure 6.26; TTHM formed over 24-hour bulk decay tests on water from Strensham WTW final water, Oversley Green BPS outlet & Tysoe DSR outlet on different sampling days versus ambient temperature.

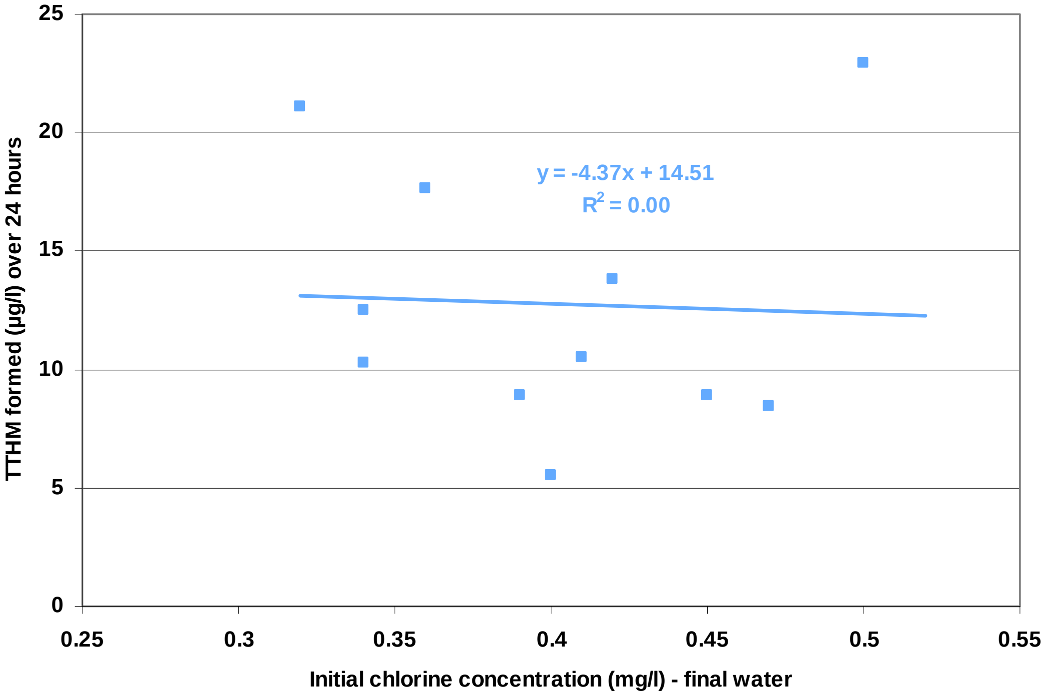


Figure 6.27; TTHM formed over 24-hour bulk decay tests on water from Strensham WTW final water on different sampling days versus initial chlorine concentration.

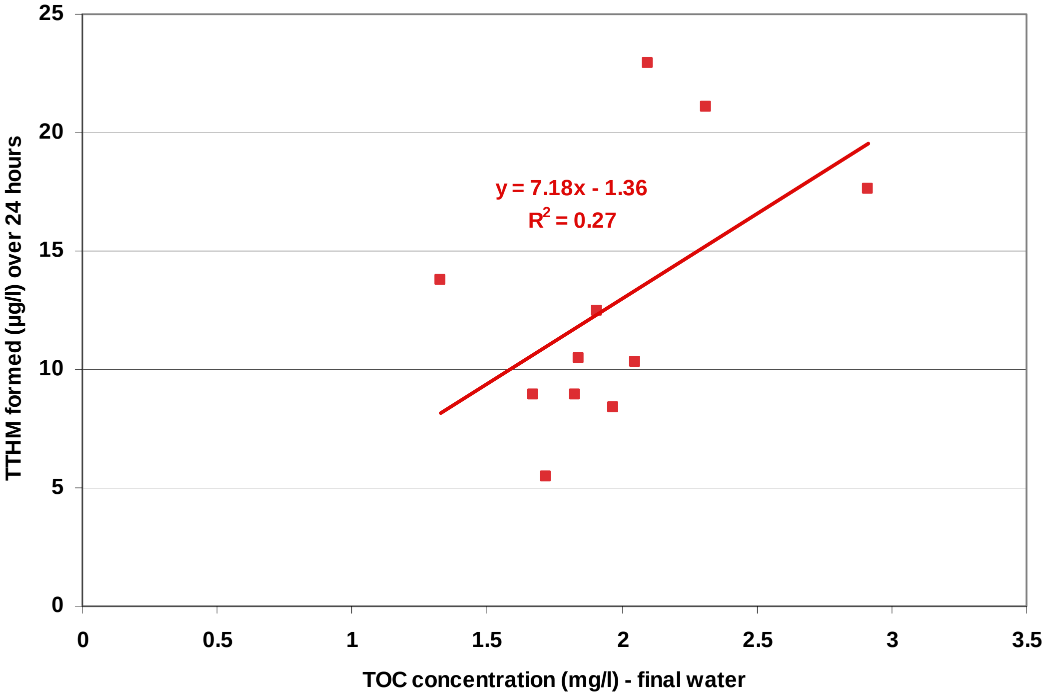


Figure 6.28; TTHM formed over 24-hour bulk decay tests on water from Strensham WTW final water on different sampling days versus TOC concentration.

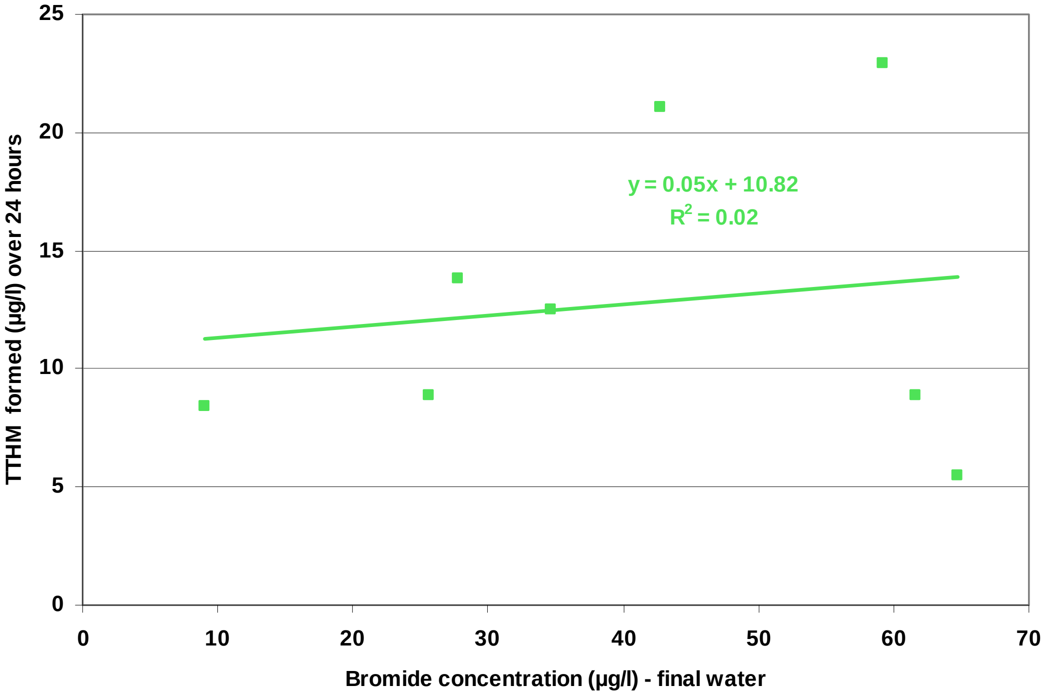


Figure 6.29; TTHM formed over 24-hour bulk decay tests on water from Strensham WTW final water on different sampling days versus bromide concentration.

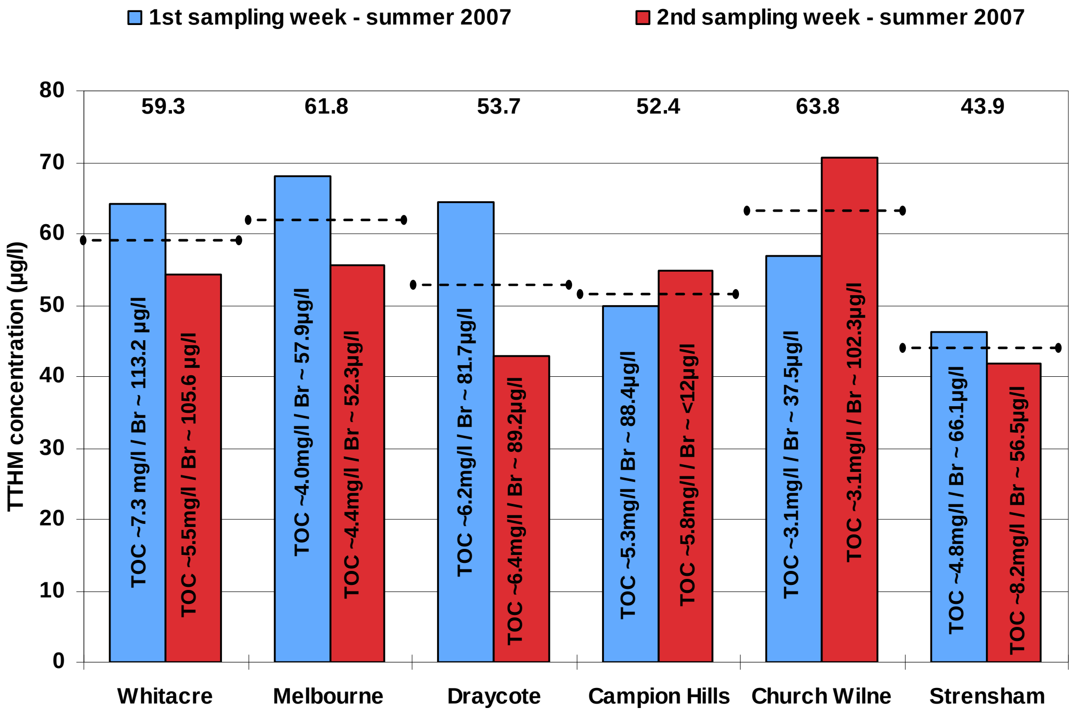


Figure 6.30; TTHM concentrations formed after 2-hour bulk decay tests on raw water sampled at each of the six WTWs on the two summer 2007 sampling weeks. All tests performed at 15°C, at ambient TOC / bromide concentrations (displayed) and an initial chlorine concentration of 1.7 mg/l.

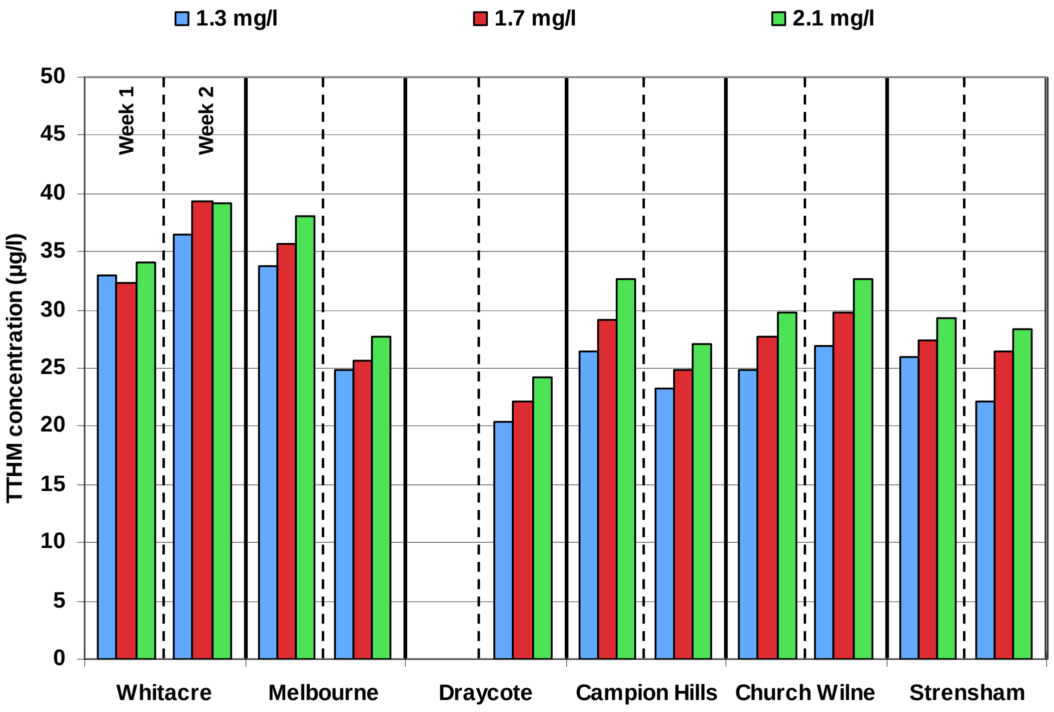


Figure 6.31; TTHM concentrations formed after 2-hour bulk decay tests on water sampled at post-GAC sampling point at each of the six WTWs on the two summer 2007 sampling days (C_0 variation). All tests performed at 15°C, at ambient TOC and bromide concentrations.

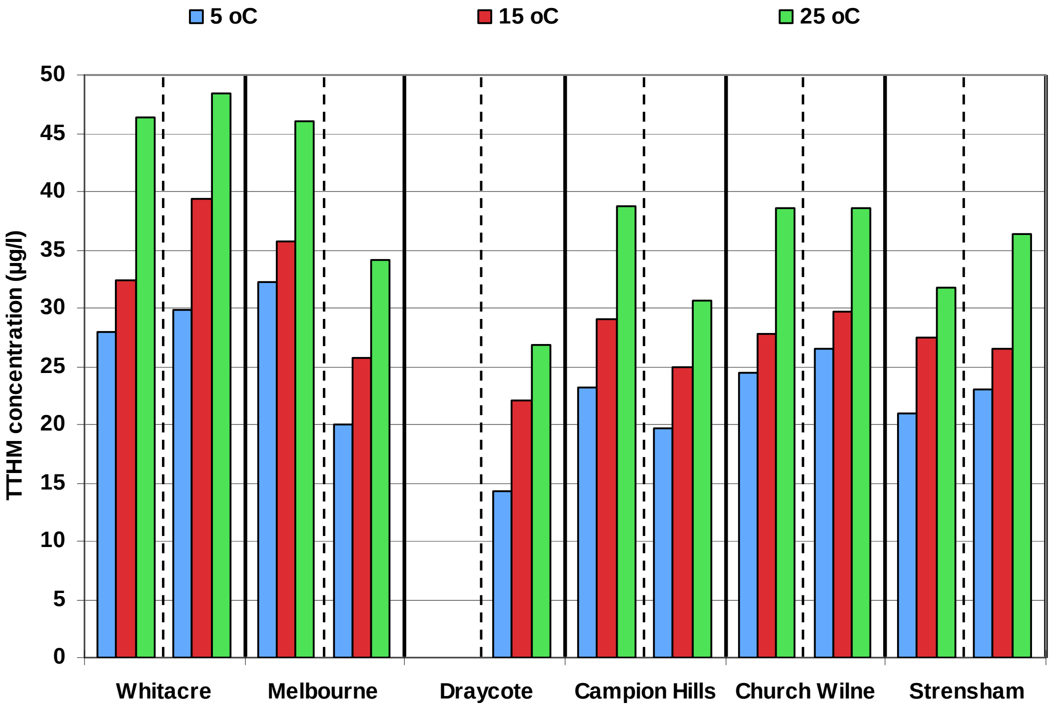


Figure 6.32; TTHM concentrations formed after 2-hour bulk decay tests on water sampled at post-GAC sampling point at each of the six WTWs on the two summer 2007 sampling days (temperature variation). All tests performed at a C_0 of 1.7 mg/l, at ambient TOC and bromide concentrations.

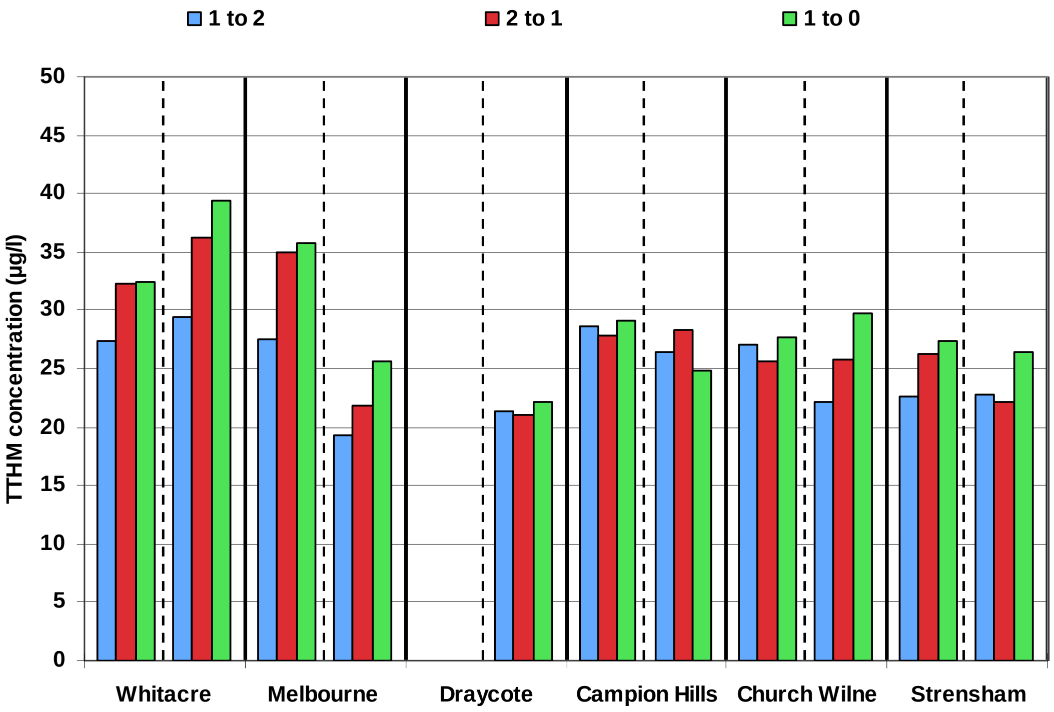


Figure 6.33; TTHM concentrations formed after 2-hour bulk decay tests on water sampled at post-GAC sampling point at each of the six WTWs on the two summer 2007 sampling days (sample water dilution variation). All tests performed at a temperature of 15 °C, and a C_0 of 1.7 mg/l.

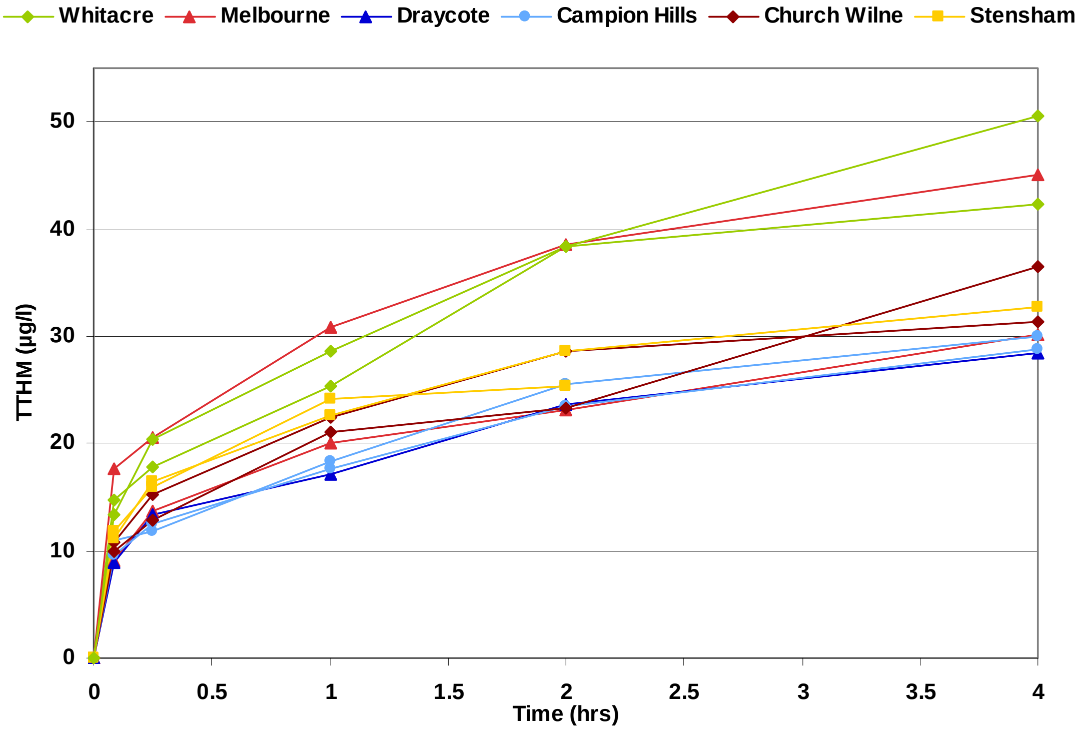


Figure 6.34; TTHM concentrations formed at selected times through the 4-hour bulk decay tests (at ambient conditions) on post-GAC waters of the six WTWs on the two summer 2007 sampling weeks.

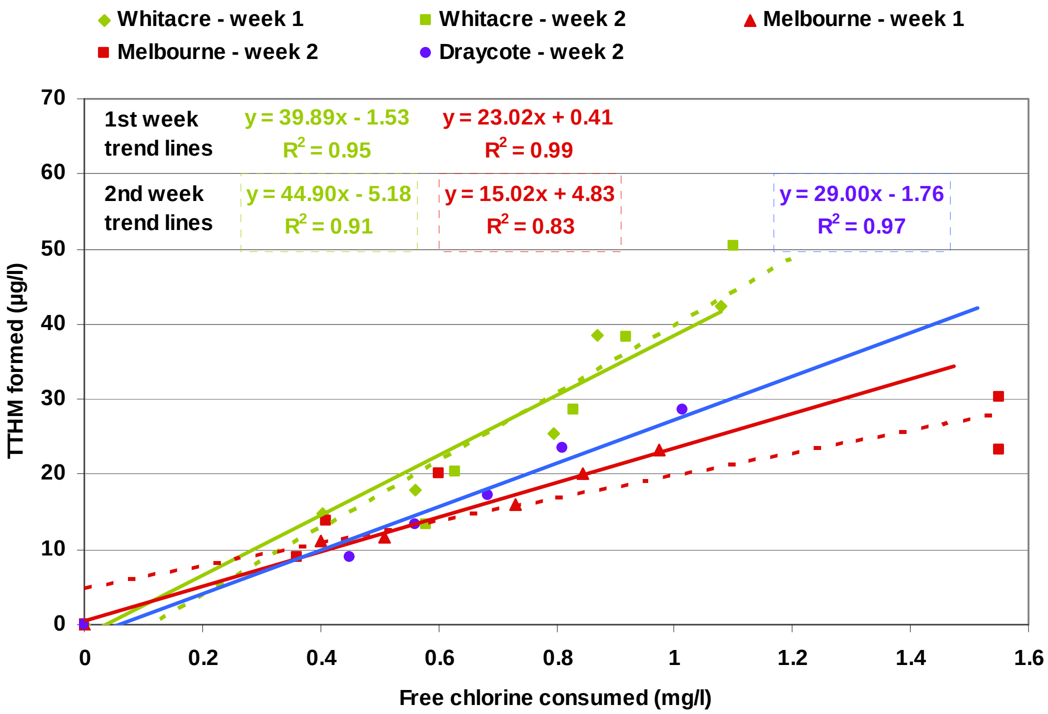


Figure 6.35; Free chlorine consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Whitacre WTW, Melbourne WTW and Draycote WTW. Dashed lines second sampling week.

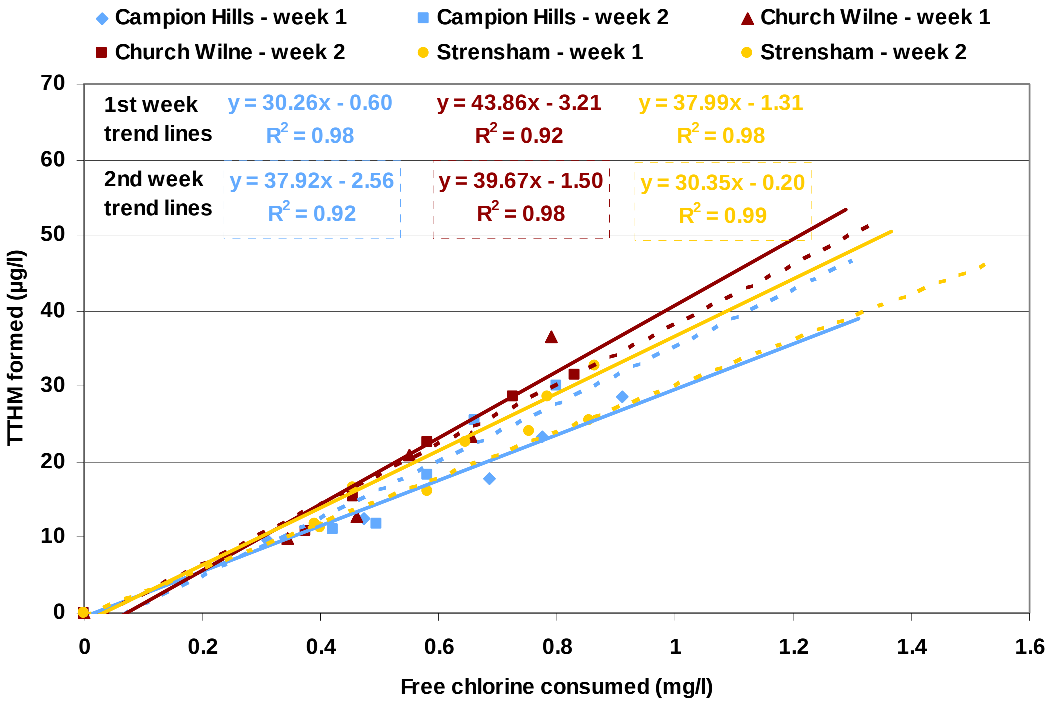


Figure 6.36; Free chlorine consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Campion Hills WTW, Church Wilne WTW and Strensham WTW. Dashed lines second sampling week.

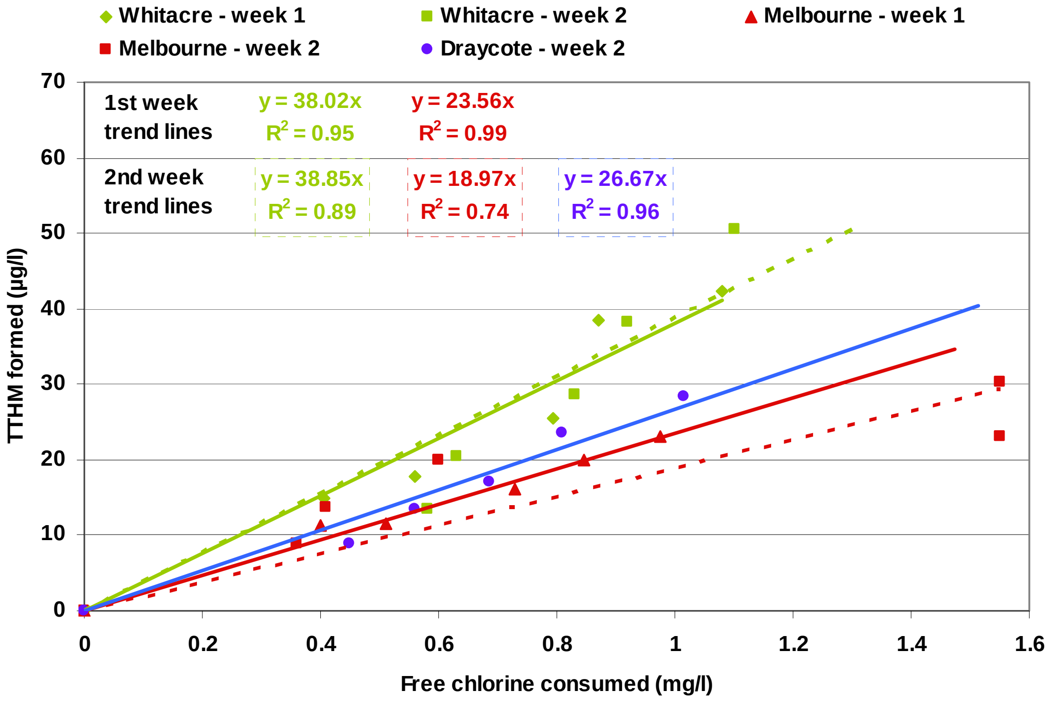


Figure 6.37; Free chlorine consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Whitacre WTW, Melbourne WTW and Draycote WTW, linear trend lines fitted through the origin. Dashed lines second sampling week.

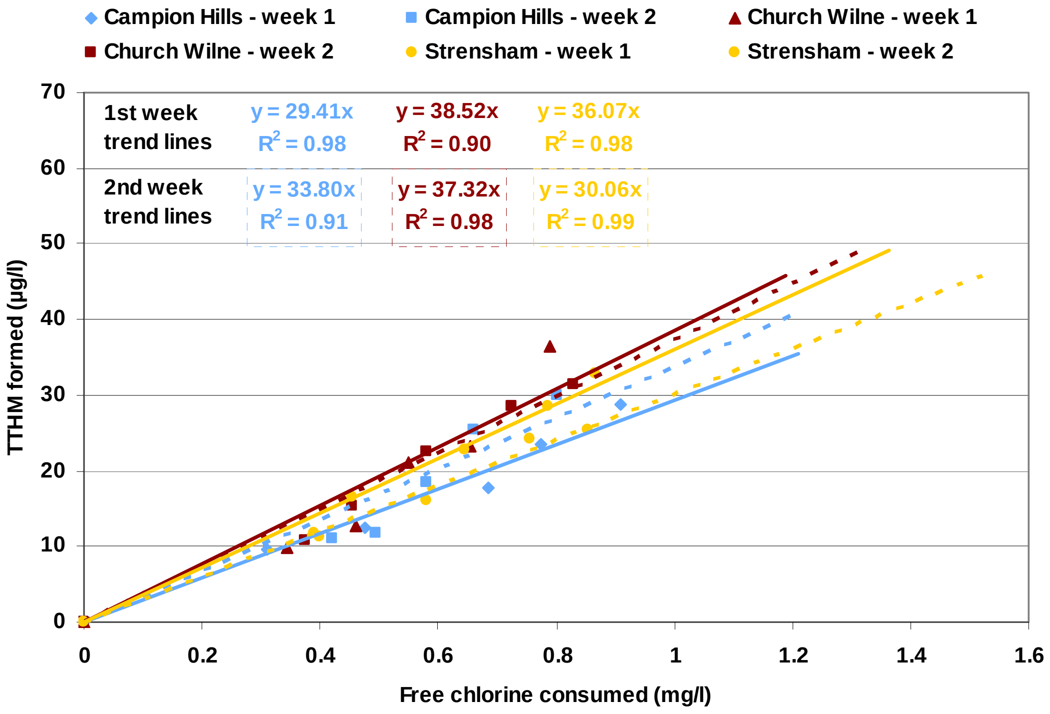


Figure 6.38; Free chlorine consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Campion Hills WTW, Church Wilne WTW and Strensham WTW, linear trend lines fitted through the origin. Dashed lines second sampling week.

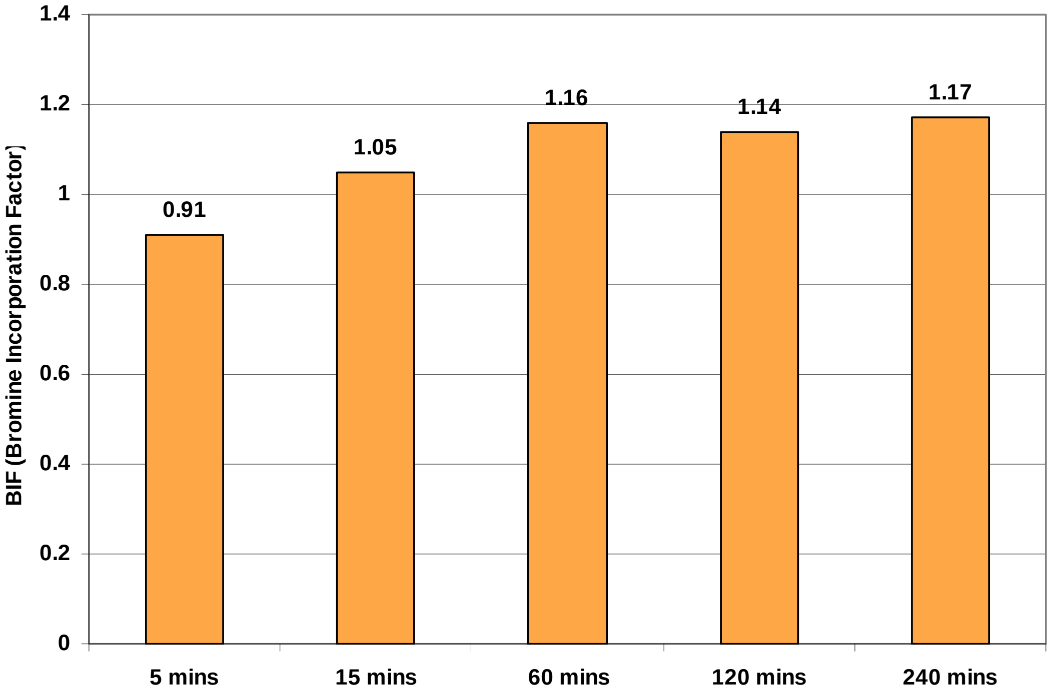


Figure 6.39; Average BIF values over different time intervals during the 4-hour contact tank simulation tests.

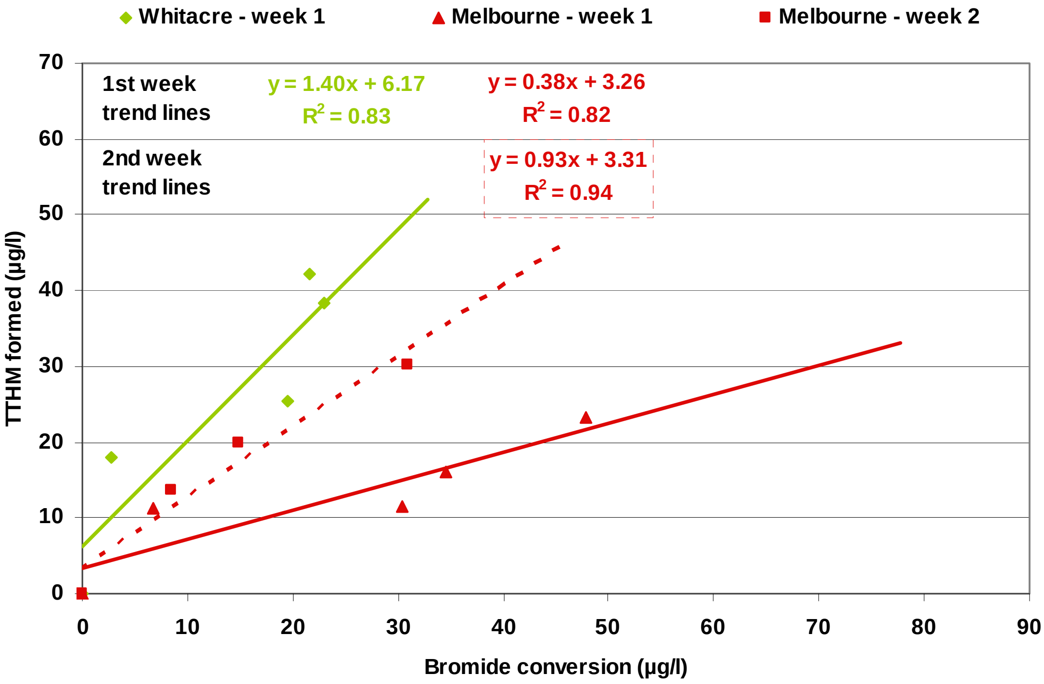


Figure 6.40; Bromide consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Whitacre WTW and Melbourne WTW. Dotted trend lines second sampling week.

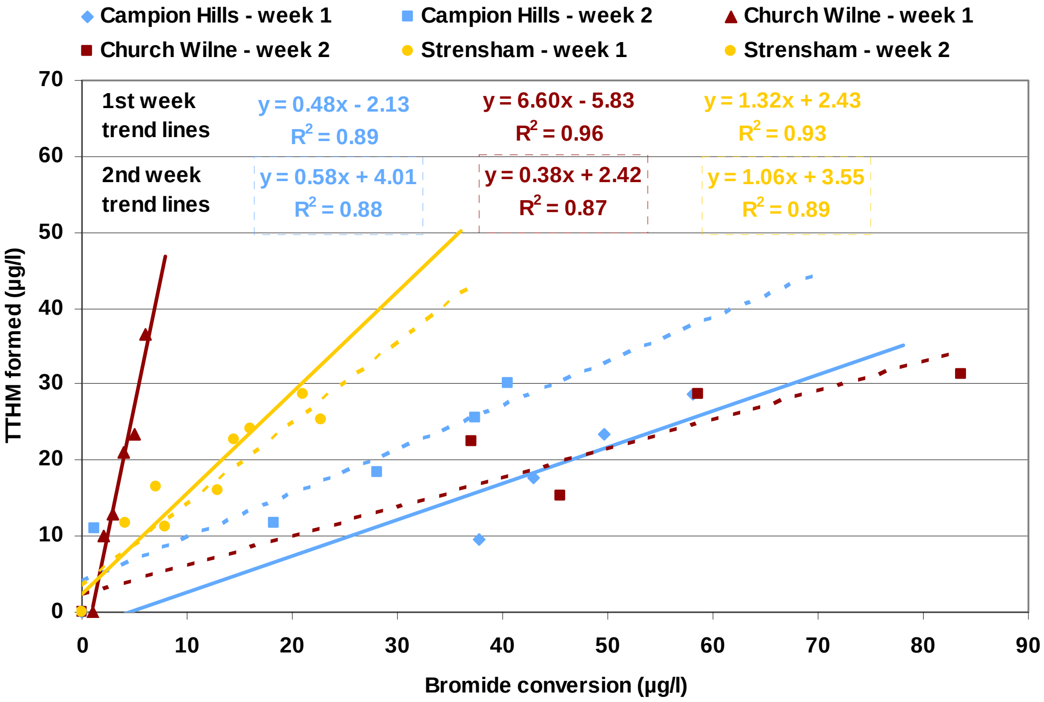


Figure 6.41 ; Bromide consumed versus TTHM formed at time intervals (5, 15, 60, 120, 240 minutes) through 4 hour bulk decay tests at Campion Hills WTW, Church Wilne WTW and Strensham WTW. Dotted trend lines second sampling week.

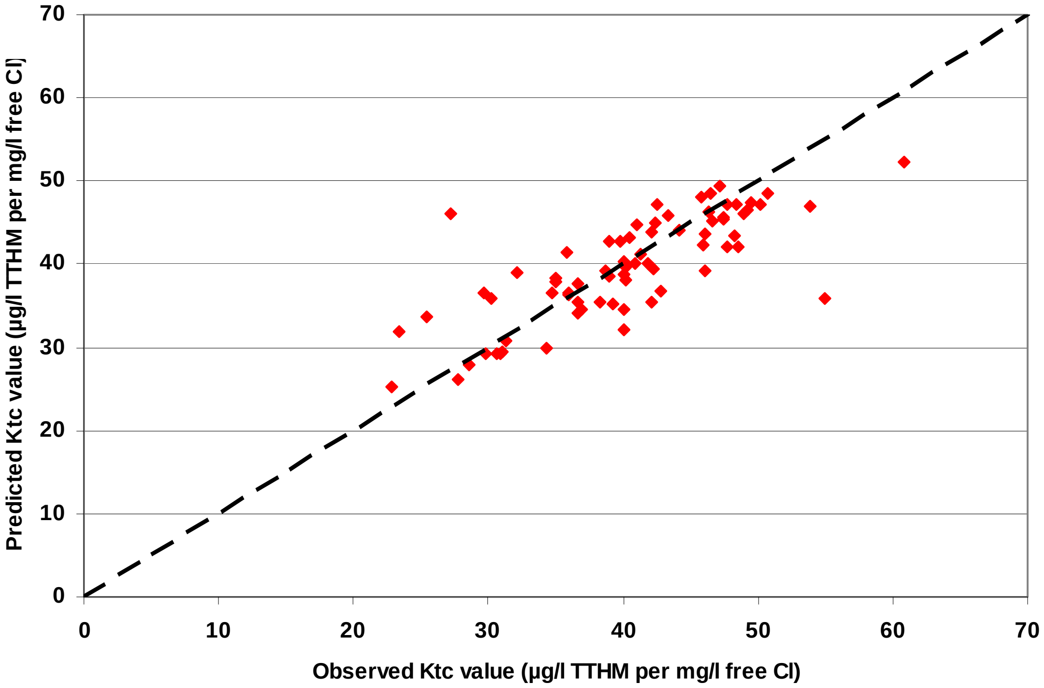


Figure 6.42; Observed versus predicted K_{TC} values using each of the six WTW individual predictive equations. Not including dilution data.

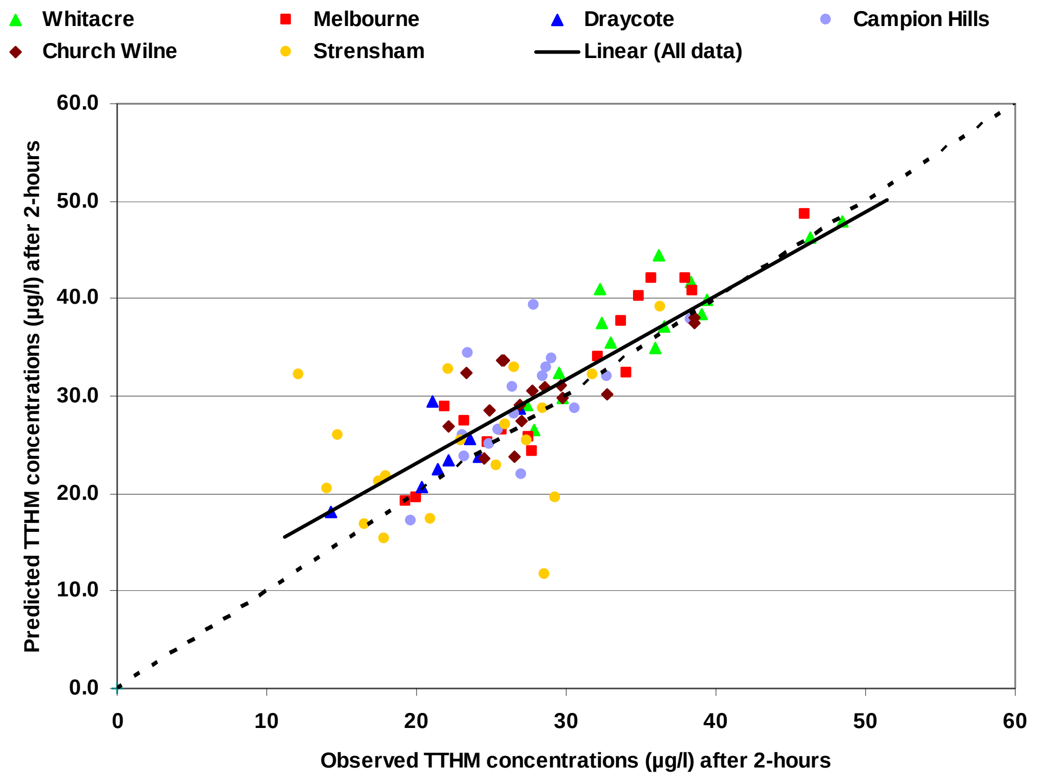


Figure 6.43; Observed versus predicted TTHM concentrations after 2-hours using predictive K_{TC} values equations in combination with the two stage chlorine decay modelling equations. All six WTWs.

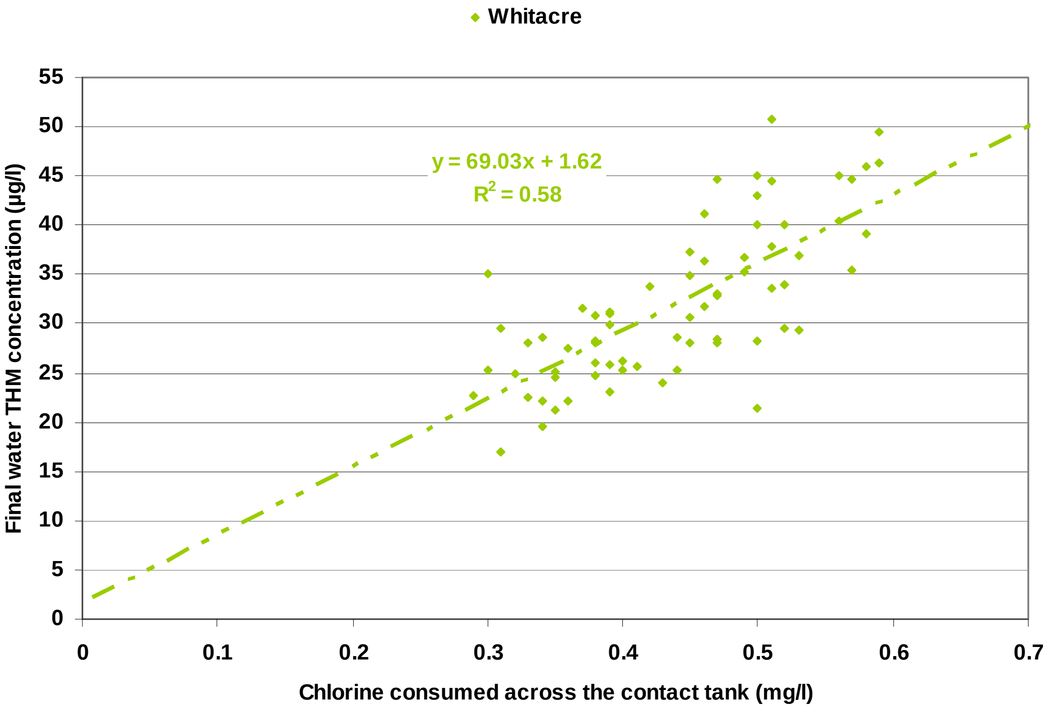


Figure 6.44; Final water THM concentrations versus the decline in free chlorine concentrations between the pre- & post-contact tank sampling points on same days. Based on STW data between October 2006 – October 2008 for Whitacre WTW.

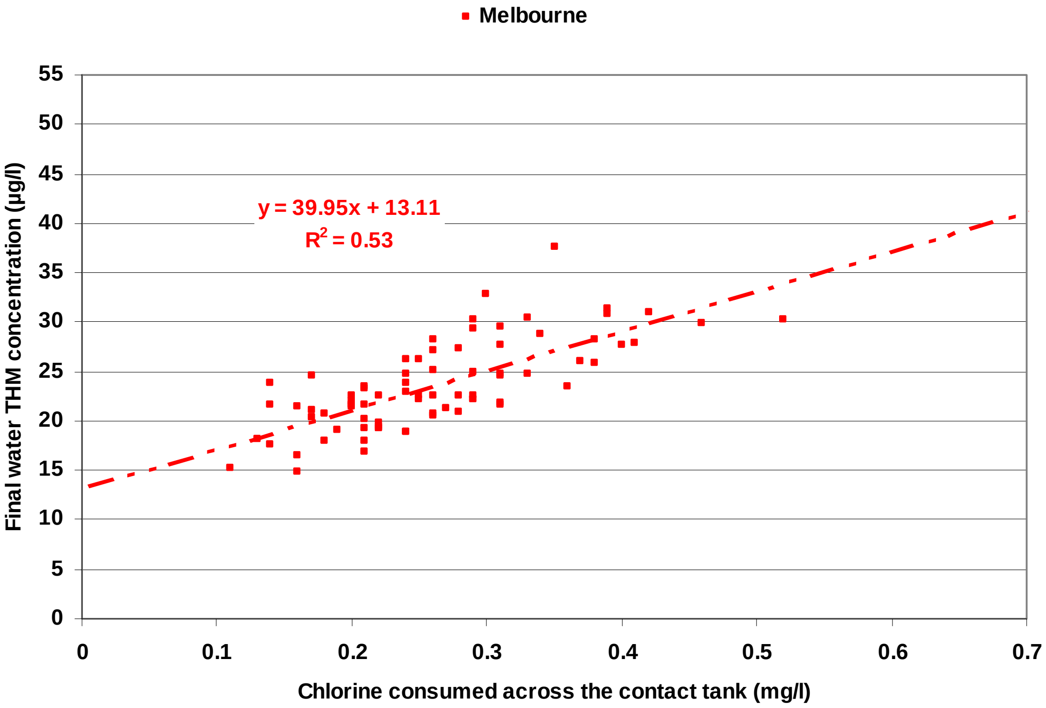


Figure 6.45; Final water THM concentrations versus the decline in free chlorine concentrations between the pre- & post-contact tank sampling points on same days. Based on STW data between October 2006 – October 2008 for Melbourne WTW.

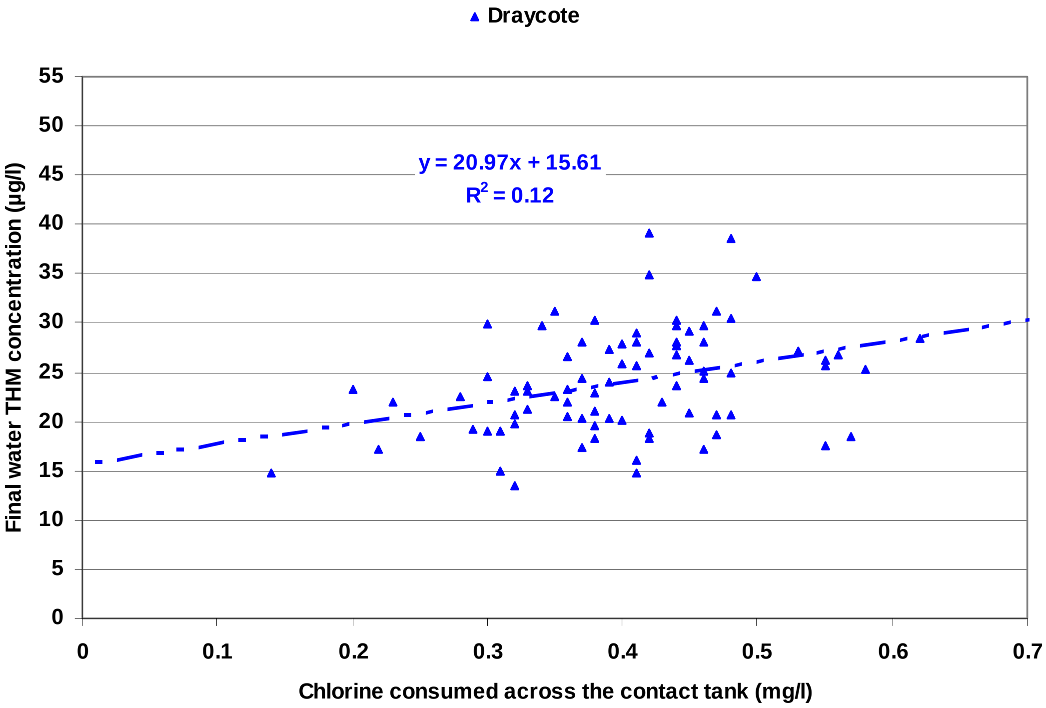


Figure 6.46; Final water THM concentrations versus the decline in free chlorine concentrations between the pre- & post-contact tank sampling points on same days. Based on STW data between October 2006 – October 2008 for Draycote WTW.

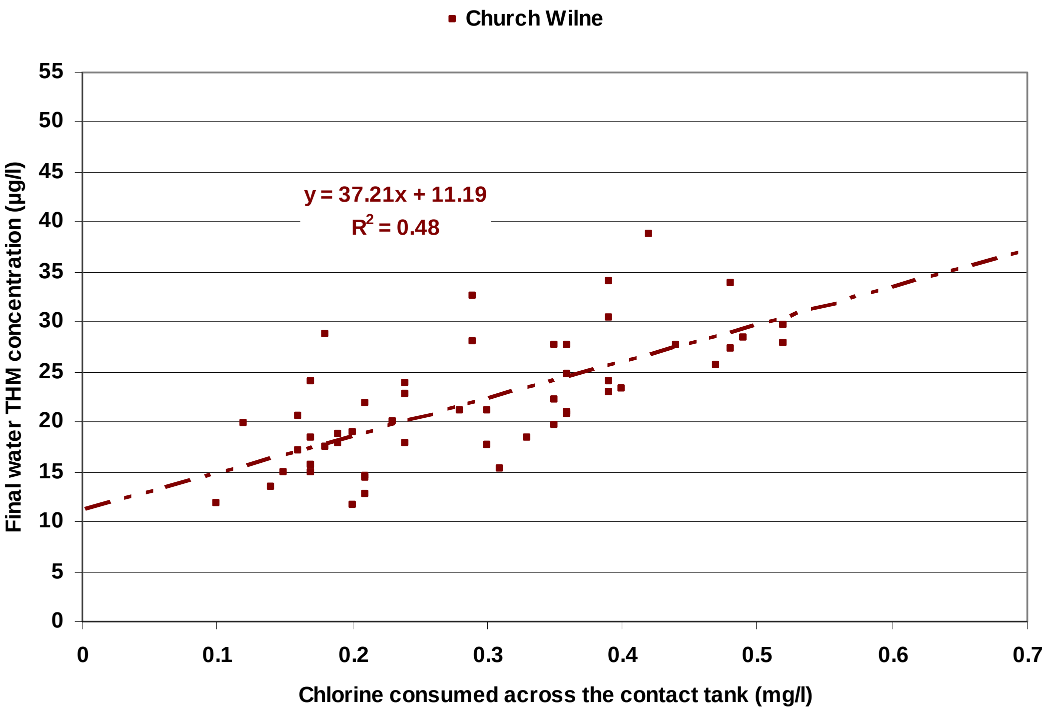


Figure 6.47; Final water THM concentrations versus the decline in free chlorine concentrations between the pre- & post-contact tank sampling points on same days. Based on STW data between October 2006 – October 2008 for Church Wilne WTW.

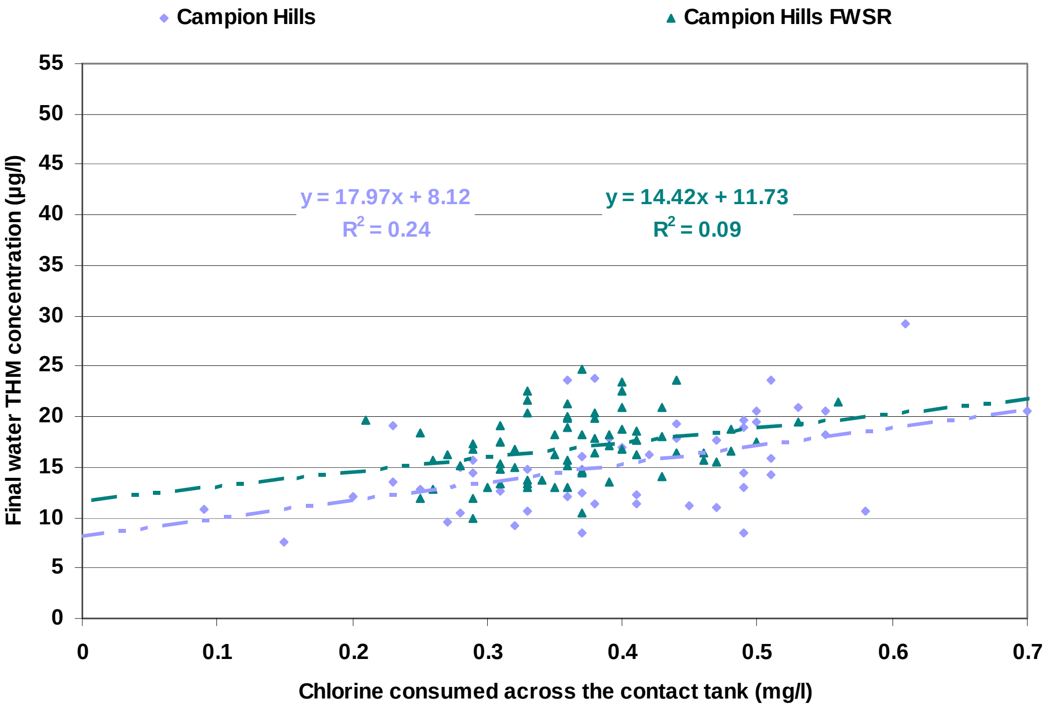


Figure 6.48; Final water THM concentrations versus the decline in free chlorine concentrations between the pre- & post-contact tank sampling points on same days. Based on STW data between October 2006 – October 2008 for Campion Hills WTW. Additionally shown on plot is the similar calculation across the FWSR.

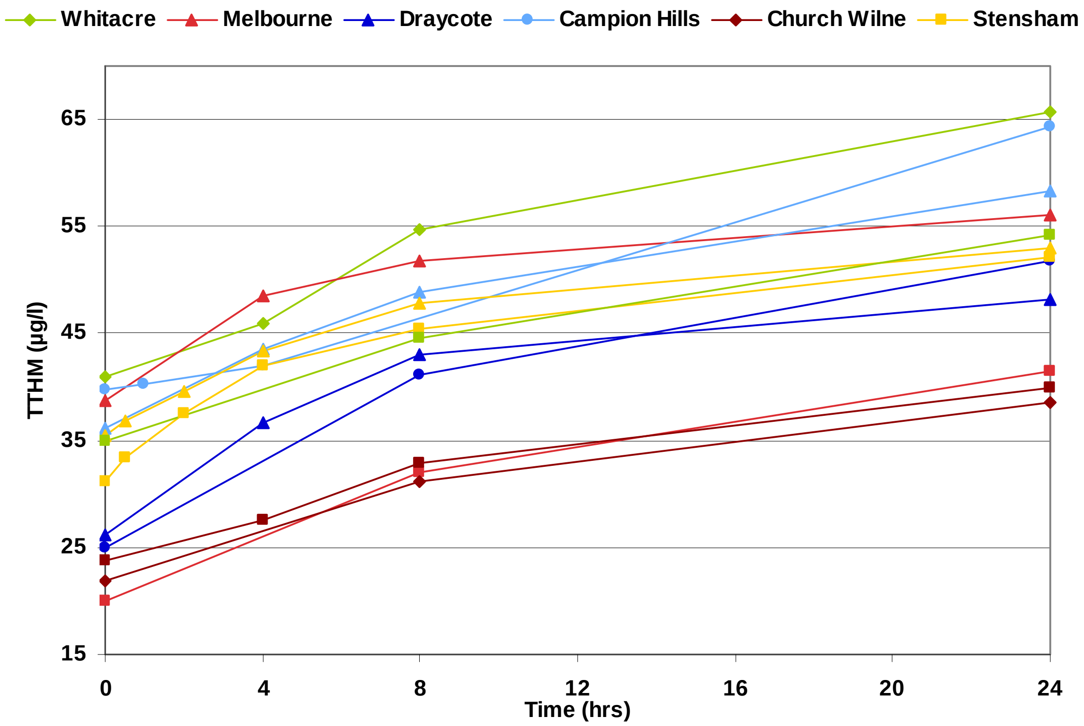


Figure 6.49; TTHM concentrations formed at selected times through the 24-hour bulk decay tests (at ambient conditions) on final waters of the six WTWs on the two summer 2007 sampling weeks.

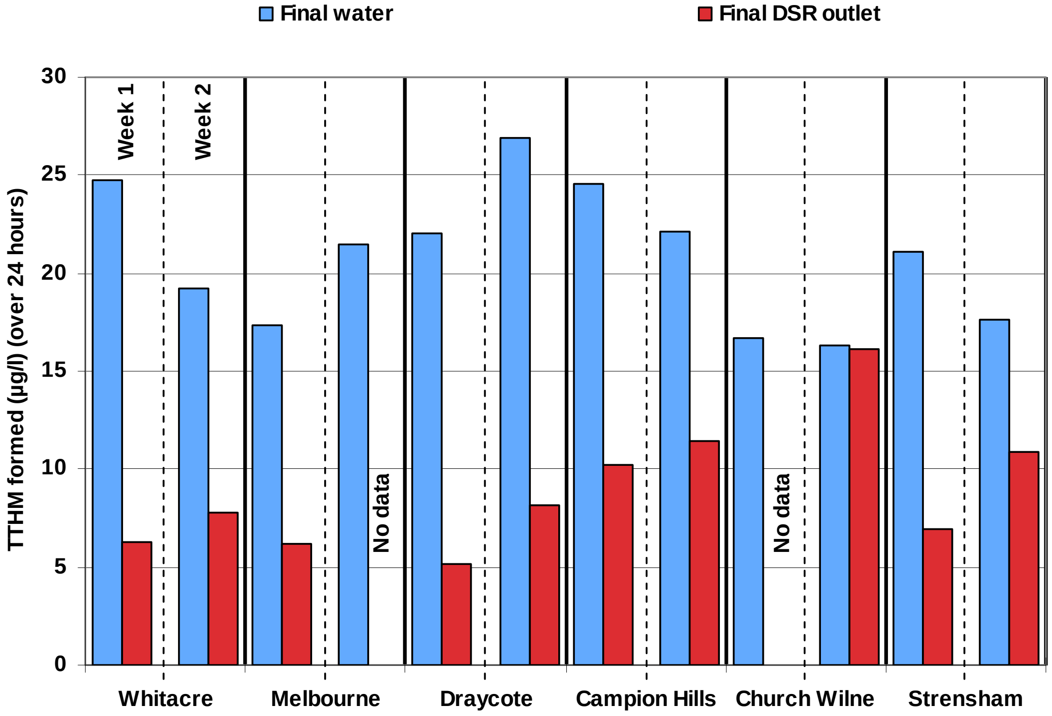


Figure 6.50; TTHM concentrations formed over 24-hour bulk decay tests on final waters and final DSR outlet water at each of the six WTWs on both summer 2007 sampling weeks.

Chapter 7 Modelling and management techniques

7.1 Introduction

Previous chapters investigated several aspects of THM formation and chlorine decay, demonstrating both to be inherently complicated and affected by a wide range of variables. In order to improve the management of the two processes, whilst ensuring regulatory safe and palatable drinking water to the customer, an holistic view of the interrelationships between water quality parameters is required.

Predictive models for THM formation and chlorine decay offer a number of economical and operational benefits in the design and management of drinking water supply systems (Sadiq & Rodriguez, 2004; Woolschlager *et al.*, 2005; Chowdhury *et al.*, 2009). A view of the predicted water quality in the system exposes areas of risk and highlights any significant fluctuations from those predictions (Hallam, 1999). This allows for operational changes to be made on a proactive, rather than a passive response basis.

This chapter draws together the understanding and knowledge gained from previous chapters with the intention of providing an economical, user friendly model capable of predicting THM formation and chlorine consumption from raw water to customer tap. The construction of the model is explained, its accuracy and limitations illustrated, and its applicability to a range of potential operational scenarios investigated. Its suitability and adaptability to other WTW and supply operations is then considered.

The work in this chapter focuses on objectives (iv) and (v) from Chapter 1;

- ***To consolidate the analysis into a cost-effective, spreadsheet model that can be practically applied in operational circumstances, enabling the user to enter prevailing water quality and WTW operational characteristics to predict chlorine use and THM formation from source water to customer tap.***

- ***To apply and critically evaluate the proposed model for one of the supply systems studied, thus identifying mitigation strategies for the management of THMs.***

7.2 Model description

7.2.1 General

The model has been based on Strensham WTW and the Shipston area of its associated distribution system. It combines the analysis of data collected from sampling days and concurrent laboratory tests, supplemented and supported by the routine monitoring samples taken by STW. Where necessary appropriate literature values for certain parameters have been adopted.

The model is divided into three interlinking MS Excel® worksheets; the model input sheet (where the raw data is input by the user), the calculation sheet (where calculations via inbuilt equations are made), and a model results sheet (where the results from the model are presented in tabular and graphical forms).

7.2.2 User entered inputs

The user has the option of entering retention times through the WTW and the distribution system into the model via the model input sheet. As an initial guide the entered values for the Strensham WTW model were based on average flows. These retention times in WTW unit processes and DSRs were determined from flow and design data. Travel times in pipes were taken from all-mains models supplied by STW.

The user enters raw water temperature, TOC and bromide concentrations at the head of the WTW. Temperature remains constant through the WTW and distribution system, which is consistent with the negligible observed variation in Chapter 4. The model accounts for the decrease in TOC and bromide concentrations though the WTW on a straightforward percentage removal basis across the clarifiers, RGFs, and GAC unit processes based on data from STW databases, fortified spatially by the data collected on sampling days.

7.2.3 Chlorine decay

Chlorine can be added to the water in the model at the inlet to unit processes and pipes only (therefore, if operationally chlorine is added at the outlet to a service reservoir or booster station, in the model chlorine is added at the inlet of the pipe immediately downstream of the DSR).

In the absence of pre-chlorination, to replicate the rapid initial consumption of chlorine across the contact tank, two time periods are considered (described in section 5.6.1). In the initial five minute period, the rapid initial decay of chlorine is modelled by a percentage drop in the set-point pre-contact tank free chlorine concentration (determined through applying the factor, p). In the latter period, chlorine decay is modelled using first-order reaction kinetics.

In both periods the SPSS derived equations of the form displayed in equation 5.4 are applied to determine the relevant factor and bulk decay constant, dependent on contact time, temperature, initial free chlorine, TOC and bromide concentrations. The user inputted retention time establishes the selection of the most appropriate of the four time period equations (5-30, 5-60, 5-90 or 5-120 minutes) to calculate the bulk decay constant for the latter period. This is subsequently applied to the five-minute concentration to determine the free chlorine concentration at the outlet of the contact tank.

Simulation of de-chlorination is represented by a user entered set point chlorine concentration at the tank outlet. The drop in free chlorine concentration is calculated by the chlorine concentration at the contact tank outlet minus this set-point value, and is not included in the calculation of cumulative chlorine consumed and the THM formation calculations as described in section 7.2.4.

Despite the fact that it is not practised currently at the WTWs studied, the model has the capability to simulate pre-chlorination to provide the user with a scenario testing facility. Pre-chlorination can be simulated at the pre-clarification stage, entered into the model as a set point free chlorine concentration. Averages of the laboratory observed bulk decay constants are then applied across the clarification and filtration unit processes, feeding into the TTHM calculations. Any chlorine present in the water downstream of these unit processes is assumed to be subsequently removed by the GAC process, and the model proceeds thereafter to disinfection as normal.

Both K_B and K_W are derived from a combination of sample and test data (detailed in Chapter 5), supplemented with literature values when data availability is limited.

7.2.4 THM formation

The model is constructed using the basic philosophy that of the amount of chlorine consumed by the bulk demand of the water, a proportion is used in forming TTHM (via K_{TC} values).

Across the contact tank the estimation of K_{TC} values with respect to C_0, temperature, TOC and bromide concentration is incorporated within the predictive equation developed in section 6.6.2. The K_{TC} value is calculated via the values of these parameters at the pre-contact tank stage and is applied to the chlorine consumed in the two stages described in the preceding section 7.2.3. Separate K_{TC} values are then subsequently applied post-dechlorination to the amount of chlorine consumed due solely to bulk decay (based on the averages of observations made on sampling days).

7.3 Limitations of the model

The model accounts for the decrease in TOC through the works on a percentage removal basis. This does not allow for changes in the removal of organics with changing coagulant dose, or age of GAC, bar using a different percentage guide. An attempt was made to link coagulant dose and the percentage removal across the WTW was made in section 4.4.1, and future work could help to improve this relationship with respect to clarification conditions and other unit processes.

Travel times through the model are based on average retention times across pipes and service reservoirs. In all cases tracer experiments can be performed if further clarification is required and the results incorporated to reflect changes under different flow and operating conditions. This has been found to be relatively easily achieved in distribution systems using modest spikes of chlorine (Powell, 1998; Hallam, 1999).

The model predicts TTHM, and the breakdown of the THM species is based on typical observations made in Chapter 6 at selected points in the model. A relationship between bromide concentrations and brominated THM species was observed (Chapter 4 and 6). Future work should attempt to clarify the complexity of this issue as it was beyond the scope of the present study.

Under the conditions of pre-chlorination in the model, the reactivity of the water downstream of this dosage point makes no allowance for the preceding contact with chlorine and the decline in the waters reactivity (e.g. with the calculations applied across the contact tank). The model has been developed using water in the absence of prechloriantion conditions. Due to the current attitude towards the generation of DBPs it is unlikely that prechlorination would become prominent in the future, hence the reason why the model does not give too much concern to this issue. Further analysis would again help the model's adaptability to this situation.

There is no account taken for any potential change in k_W within the system with respect to temperature, initial chlorine concentration and the velocity of the water, each of which are known to have some impact (section 2.7).

Future work could include the possible use of a link between the organic precursor concentrations and UV_{254} absorbance at the WTW to enable online monitors to be used to input the required organics concentrations into the model for calculating chlorine decay and THM formation.

7.4 Model validation

To ensure that the conceptual model provides a useful evaluation of the current operational conditions at the WTW and distribution system, the model was applied to a set of indicative mean parameter values (referred to in the remainder of the chapter as the ‘reference model’ values) and compared against observed values from sampling and routine monitoring data.

Raw water TOC and bromide concentrations were assumed as 5 mg/l and 80 µg/l, respectively. A temperature of 15 °C was applied. The TOC removal rates of 35 %, 9 % and 15 % across the clarification, RGFs and GAC unit processes, were applied from the average percentage removals observed on the sampling days. The set-point pre-contact tank free chlorine concentration was assumed to be 1.9 mg/l with the water de-chlorinated at the contact tank outlet to a concentration of 0.45 mg/l. In the selected stretch of the Strensham to Shipston distibution system both DSRs (Brailes and Tysoe) were assumed to be chlorinated at the outlet to a concentration of 0.2 mg/l. Chlorination was also assumed at the outlet to the first (Oversley Green) but not the later (Feldon) of the two BPS (to a concentration of 0.3 mg/l). All concentrations reflect typical summer chlorine dosages observed at these points.

The results were checked against the observed values at select points through the distribution system and also against values calculated manually through the various calculation stages (to ensure there were not any errors in the operations of the model). Figure 7.1 displays the model predicted TTHM and chlorine concentrations through the WTW and distribution system along with the sampling data from the 04.06.07 sampling day (which had water quality parameter concentrations closest to the reference model values: raw water TOC ~ 4.76 mg/l / bromide ~ 66.1 µg/l / temperature ~ 18.2 °C). It can be seen that the predicted and observed THM concentrations at the outlet of the final DSR are similar (compared to summer averages), and that the free chlorine and THM concentrations follow a similar path through the majority of the WTW and distribution system. The model is seen to slightly under-predict TTHM concentrations across the contact tank and the in the early stages of distribution, but this is likely to be attributable to the lower reference model temperature. However with increased analysis and fine tuning of the model, these discrepancies can be addressed and eliminated.

Significantly, the model indicates that approximately 45 % of the TTHM found at the end of the distribution system is formed at the WTW, which is in agreement with observations from the sampling days (Figure 4.39) and also from routine STW data (Figures 4.40 and 4.41). A large fraction of the TTHM is also produced quickly across the contact tank, which was another key feature observed in preceding chapters.

In order to assess the relative importance of the main inputs into the model, a sensitivity analysis was performed, where the three main raw water quality parameters (temperature, TOC concentration, and bromide concentration) were individually varied by ± 30 % (whilst other parameter values were held constant at reference model values) to observe the effect on TTHM formation. For each of the parameters this 30 % variation reflected realistic operational variation and was therefore deemed acceptable for use.

The results are displayed in Figures 7.2, 7.3 and 7.4 for the variation in TOC, temperature, and bromide, respectively. It is evident that the modelled THM concentrations reflect a response to each variation of the independent parameters, with the magnitude reflecting the relative contribution of each parameter in chlorine decay and THM formation in the modelling process.

The effects on TTHM concentrations at the WTW final water and customer tap are summarized in Table 7.1. Raw water TOC concentrations are shown to be the most significant factor in the formation of THM in the model, followed by temperature and raw water bromide concentrations. The + 30 % and – 30 % variation in raw water TOC concentration led to + 27 % and – 29 % change in the customer tap TTHM concentrations, respectively. Whereas, the + 30 % and – 30 % variation in raw water bromide concentration led to smaller + 12 % and – 16 % changes in the customer tap TTHM concentrations, respectively.

7.5 Application to operational scenarios and implications to THM management

In the pursuit of THM management there are a number of options available for the water supply system operator (see section 2.12). The most feasible of these, both economically and operationally, are;

- Source water management;
- Precursor removal at the WTW;
- Changes to chlorination practices at both the WTW and distribution system;
- Changes to distribution system retention times and storage practices.

In this section the viability of these management options are discussed and the model is applied to a range of operational circumstances to investigate their potential effects on the formation of TTHM and chlorine consumption through the WTW and distribution system.

7.5.1 Source water management

Observations from many countries around the world in the past 10 – 20 years indicate rising natural organic matter concentrations in water sources due to issues such as global warming, changes in soil acidification, increased drought severity and more intensive precipitation events (Fabris *et al.*, 2008). Additionally, with increasing demand on current sources, there will inevitably need to be some compromises in the water quality of both existing and new water sources (Roberts, 2004).

Chapter 4 demonstrated the considerable variability in organics and bromide concentrations in the raw water at Strensham WTW, attributed to the direct raw water abstraction from a river source. To investigate the potential magnitude of these effects due to future changes, the two parameters were isolated for investigation using the model, whilst other reference model values were held constant.

Figure 7.2 displays the variation of TTHM formation and chlorine consumption through the WTW and distribution system using the lower and upper bounds of the observed raw water TOC concentrations (2 mg/l and 10 mg/l, respectively). An increase of raw water TOC concentration was seen to lead to a significant rise in TTHM concentrations, with the principal rise occurring at the WTW. The effect in the distribution system is less prominent. As an approximation, roughly 10 µg/l of additional TTHM is formed by the customer tap for each additional 1 mg/l of TOC in the raw water in the model.

The variation in TTHM concentrations is not as significant for the change in raw water bromide concentrations (Figure 7.3), with TTHM concentrations at the end of the distribution system being within 10 µg/l of each other with the change in bromide concentrations from 30 µg/l to 140 µg/l in the raw water. Although the model does not implicitly derive the effects of the bromide / TOC ratio, explicitly the effects are accounted for in the configuration of the equations.

TOC and bromide were shown to be high and low flow critical, respectively. It is therefore unlikely that both would be consistently high at corresponding times of the year. A potential management solution to dampen the effects on THM formation of sudden peaks in river water concentrations of both these two parameters would be to introduce some measure of raw water storage. As shown at the other investigated WTWs (each with some degree of storage), the variation in raw water quality parameter concentrations entering the WTW is narrowed with the length of storage (section 4.6).

WTW management should also recognize a need to be flexible to other external factors. Temperature may not vary significantly spatially, but temporal variation can be significant. At Strensham WTW raw water temperatures were observed to range between 4 and 25 °C (Figure 4.14). The model was run to represent this variation (Figure 7.4). Increased water temperature was observed to increase the rate of TTHM formation and also resulted in a greater decay of chlorine. TTHM concentrations at the final water increased by 131 % (17.5 µg/l) with the change from 4 to 25 °C. In practical water treatment, the temperature cannot be controlled. However, the temperature dependence of chlorine decay and THM formation leads to the possibility of varying treatment processes to affect other parameters between warm and cold season, thus minimising costs (Hua, 1999).

The model was then applied to a ‘critical conditions’ scenario, where the worst case conceivable with respect to TTHM formation was investigated. Temperature was shown in both Chapters 4 and 6 to be strongly related and significant to THM formation at both the WTW and distribution system. Applying a high temperature in the model, it is probable that bromide concentrations in the River Severn would be high, reflecting the potentially low river flow. With high temperature it could also be expected that chlorine concentrations both at the WTW and distribution system would be high, to counter act problems associated with microbial activity. It is also feasible, (for the purpose of applying critical conditions in the model) that TOC concentrations would remain at there average ‘reference value’. Therefore, a temperature of 25 °C, bromide concentration of 250 µg/l, and chlorine dose of 0.5 mg/l (at each point typically chlorinated in distribution system) were applied in the model (Figure 7.5). With all these factors contributing to TTHM formation the model gave a TTHM concentration at the end of the distribution system of 102 µg/l (thus exceeding the MCL), with the minimum chlorine concentration occurring in the system of 0.08 mg/l.

7.5.2 Precursor management

Although raw water organics and bromide concentrations are beyond the control of the WTW manager, a feasible strategy is the reduction of precursors prior to chlorination to their lowest practicable level. Without large amounts of capital expenditure on new treatment processes within a WTW, options for the reduction of precursors are restricted to a number of possible upgrades to existing unit processes within the conventional treatment stream. It is essentially very difficult to achieve bromide removal through conventional treatment processes (as explained in section 4.4.2). However, improved removal of organic precursors is achievable through enhanced coagulation by increasing coagulant dosage or optimising pH and/or regenerating GAC beds more frequently. Both options are likely to incur an increase in operational expenditure and therefore need to be justified.

The simpler of these two options is through decreasing the regeneration period of the GAC beds. Previous studies have shown this to significantly increase the amount of THM precursor removal. For example, Roberts (2004) showed GAC approximately 18 months old removed between 5 and 15 % of TOC, whereas 3 month old GAC removed between 40 and 50 % of TOC. Alternatively, an increase in the coagulant dose has been demonstrated in many studies to remove an increased fraction of the organic matrix (Owen *et al*., 1993; Clark *et al*., 2001; Teksoy *et al*., 2008). In this study, estimates suggest a 1 mg/l increase in coagulant dose leads to an approximate 10 % increase in the removal of TOC between the raw and final waters at Strensham WTW (Figure 4.22). To demonstrate the potential variation in THMs as a result of unit processes efficiency, a 50 % decrease and increase in the reference model values were applied across the clarification and GAC unit processes in combination.

Figure 7.6 shows that a 50 % increase in percentage TOC removal across these two unit processes leads to the maximum amount of TTHM within the distribution system declining by 15 µg/l. Applying a 50 % increase on the other hand leads to an increase in maximum TTHM concentrations by 17 µg/l. Treatment to remove organics and inorganics in the water will also curb the rate of chlorine decay, thus allowing a higher residual to reach further into the system and persist longer. Although barely noticeable in the distribution system, due in part to the scale of the ordinate, the effect of changes in process efficiency on chlorine concentrations across the contact tank is more pronounced.

7.5.3 Chlorination practices

The chemical characteristics of water sources differ tremendously, as do, to a lesser degree, those of a single source from time to time. Effective chlorination control therefore necessitates adjustments in chlorine feed, not only to allow for the variation in water flow, but also to accommodate for the variations in water quality.

Beyond the over-riding constraint of achieving adequate disinfection, there are a number of additional factors that come into play in any strategy for the control of chlorine dosage in the WTW and distribution system. Across the contact tank, reducing the contact time is an improbable option because too short a contact time results in a lower efficiency in killing bacteria. Besides achieving adequate primary inactivation of microbial organisms, an adequate residual must also be maintained up until the periphery of the distribution system, to inhibit microbial re-growth (Boccelli *et al.*, 2003). Conversely, from a purely economical point of view, there is also a clear requirement to use the minimum dosage possible. Significant variation of chlorine concentrations at the tap is also a common cause of customer complaints.

Chapter 4 highlighted interventions in chlorine dosages in the Strensham distribution system during the summer months to help combat higher THM concentrations. A fine balance must be found when doing this to minimize TTHM formation, whilst ensuring microbiological safety of the network (which also poses its highest risk with warmer temperatures). At reference model values with an increased temperature of 25 °C, the model predicts that the minimum free chlorine concentration in the distribution system would be 0.05 mg/l towards the extremities of the system (Figure 7.4). This is well below the 0.20 mg/l that Hallam (2000) suggests is required to inhibit bacterial re-growth in a distribution system and would therefore leave the system vulnerable to bacteriological failure over extended lengths of residence time. In terms of THM management this clearly restricts the options available to distribution system operator in terms of reducing chlorine concentrations and places the emphasis on management of THM precursors at the WTW.

Besides raising or lowering the chlorine concentration at the dosing points, attention should also focus on decay within the system, and the relative contribution that wall and bulk decay components play. If the wall decay component is significantly greater than the bulk component this suggests management of the distribution system. Whereas if bulk decay exceeds wall decay, system management should focus on the water entering the system and WTW operations (Hallam, 2000). At the start of the distribution system, where the water is relatively fresh, pipes are of a large diameter and frequently maintained, the effects of bulk decay will be dominant. As the water continues through the distribution system, the water passes through more re-chlorinations, becomes less reactive, and pipes reduce in diameter as smaller volumes of water are being conveyed through them. The effects of wall decay therefore become increasingly more important with distance and focus should be placed on wall decay in such locations. Under reference model values the wall decay at the start of the distribution system accounts for 34 % of the chlorine consumed (at the end of pipe 1 or Oversley Green BPS inlet). This amount increases to 78 % by the end of distribution system (at outlet to pipe 6 or the customer tap).

Up until the broad consensus of its disadvantages with regards to excessive DBP formation, pre-chlorination was a routine practice in most surface water WTWs to aid operational problems associated with biological growth and to assist treatment efficiency. At most conventional surface water treatment plants (as was the case at Strensham WTW up until 2003 / 4) chlorine was typically added at either the raw water intake or flash mixer prior to clarification. Model results showing the impact of 1 mg/l and 2 mg/l doses of chlorine at this stage on TTHM formation are shown in Figure 7.7. The beneficial effects on TTHM formation of suspending this practice are clearly demonstrated. The majority of the applied chlorine dose is rapidly consumed across the clarification stage, as was observed in bulk decay experiments on raw water (section 5.5). Due to the large concentration of precursors in the untreated water, this leads to a large portion of THM being formed. This, in addition to the THM formed downstream, leads to the predicted TTHM concentration at the end of the distribution system (for a pre-chlorination dose of 2 mg/l) being nearly double that of the reference model concentration.

7.5.4 Effects of water residence time and distribution system practices

The residence time of water is a major factor contributing to the deterioration of water quality within the distribution system. It is a function primarily of water demand, system operation, and system design.

In addition to meeting current demands, many water systems are designed to maintain pressures and quantities needed to meet future demands or to provide extra reserves for fire fighting, power outages and other emergencies. Building distribution facilities that are large enough to accommodate future demand can in the near term increase water age as the storage volume in the constructed facility may be large relative to the present day demand. Operational practices can impact flow direction, flow velocity and hence, water age. Reservoir operations can significantly impact water age and associated water quality decay, with increased water age usually attributed to under utilization and / or poor mixing of the water.

The model was run varying the retention times for the two DSRs in the distribution system. At retention times of 50 % of the reference model for each of the DSRs, the model predicted that TTHM concentrations at the end of the distribution system would be 4 µg/l less than the reference model values (Figure 7.8). This value would probably be higher if the DSR were situated closer to the WTW where the water is more reactive still and also within systems with different characteristics. The option to reduce retention times for the purpose of reducing DBPs again requires careful consideration. A balance needs to be obtained for the need to store water for use during both normal and emergency conditions with the need to convey water quickly through the system in order to minimize residence times.

7.6 Applicability to other WTWs

As the work in previous chapters has shown, relationships between water quality parameters have been shown to be system specific. The management of THM within the WTW and distribution system is very difficult to achieve and as demonstrated in the use of the model involves a reliance on understanding of these relationships.

The management decisions of one system cannot therefore be applied to another system with different water quality and operational characteristics. Nevertheless the broad principles to help with the management of a system and also the basic structure of the model developed in this Chapter can be widely applied. With the knowledge gained of the chlorine decay characteristics and the THM productivity of the water in previous chapters, the model can be readily applied to other WTWs and distribution systems alike to provide an initial assessment of the risks of THM formation at different sites, and to identify sites and systems at risk of compliance failure. Additional samples and analysis would further enhance the accuracy of both the current and adapted models in the future.

7.6 Conclusions

- A simple, yet robust, approach to the modelling of chlorine decay and THM formation has been developed, through the use of derived chlorine decay constants and K_{TC} values for various types of waters under a range of operational conditions (described in Chapters 5 and 6, respectively).

- The modelling concepts outlined here can be seen to offer a robust, yet straightforward alternative approach to chlorine decay and TTHM formation prediction at WTWs and in distribution systems, without reliance on large expensive datasets or extensive calibration required for other models.

- The model can thus be applied to assess the chemical and microbiological risk balance under different scenarios allowing for informed decision making.

- Despite not offering a robust interpretation of the complex relationship between TOC and bromide with bulk decay and THM formation, the model has been shown to be fit for purpose. Promising results have been obtained, with model data reasonably reflecting measured data. Although some over-prediction of both processes has been found in the contact tank, results in the distribution system are more encouraging, with concentrations at the extremities being within 6 µg/l of the observed concentrations on a sampling day with similar ambient conditions to reference values applied (Figure 7.1). Relying only on the measurement of analytically undemanding parameters (in particular, chlorine and its decay with time), under appropriate circumstances this model offers advantages of simplicity and cost-effectiveness over other, more complex models.

- TOC and temperature were shown to be the most significant factors in determining TTHM concentrations in a relatively low bromide water supply system. Although temperature is an unmanageable external factor, organics removal through the WTW was shown to significantly impact the downstream concentrations of THM formed. This however comes at an extra cost, which suggests the use of different operational conditions to respond to seasonal variation.

Parameter		**TTHM formed by final water**		**TTHM formed by customer tap**	
		Concentration	**% difference**	**Concentration**	**% difference**
TOC	- 30 %	12.3 µg/l	- 40 %	32.9 µg/l	- 29 %
	5 mg/l	20.6 µg/l	-	46.4 µg/l	-
	+ 30 %	29.9 µg/l	+ 45 %	59.3 µg/l	+ 27 %
Temperature	- 30 %	14.5 µg/l	- 30 %	35.4 µg/l	- 23 %
	15°C	20.6 µg/l	-	46.4 µg/l	-
	+ 30 %	28.6 µg/l	+ 39 %	57.3 µg/l	- 23 %
Bromide	- 30 %	15.1 µg/l	- 27 %	38.7 µg/l	-16 %
	80 µg/l	20.6 µg/l	-	46.4 µg/l	-
	+ 30 %	25.4 µg/l	+23 %	52.1 µg/l	+12 %

Table 7.1; Sensitivity analysis of the three main raw water quality inputs into Strensham WTW model (± 30 % variation) and the effects on final water and customer tap TTHM concentrations.

Chapter 8 Conclusions and future work

8.1 Conclusions

8.1.1 Principal conclusions

- Average final water TTHM concentrations ranged from 16.4 to 32.9 µg/l (s.d. ~ ± 4.9 to 8.0 µg/l) over the study period (2003-8), with a significant seasonal trend evident at each of the six WTWs (a two fold increase in summer concentrations compared to winter concentrations is apparent).
- The percentage of THM concentration formed in the WTW varied between 40 and 65 % of the final customer tap value. Approximately 80 % of this THM formation at the WTW occurs across the contact tank.
- Sampling and laboratory data showed THM formation to be initially rapid followed by a more prolonged slower formation. Between 35 and 45 % of the TTHM formed in two-hour contact tank simulation tests at the six WTWs occurs within the initial five minute period of the test.

- Chlorine decay was also observed to be characterised by fast and slow reactions that are dictated by a water's characteristics and the prevailing chlorination conditions. Observations from tests on post-GAC water showed the majority of these quick reactions with chlorine occurred within the first five-minute period, with between 9 and 28 % of the initial chlorine being consumed within this period.
- Chlorine decay was observed to have a positive relationship with TOC and temperature, whereas an inverse relationship was observed with C_0 and bromide.
- A two stage process to modelling chlorine decay has been developed and its application to a range of test conditions showed encouraging results with concentrations approximately ± 0.05 mg/l (± 4.2 %) from the observed concentrations after 60 minutes and ± 0.1 mg/l (± 6.5 %) after 120 minutes.
- These equations were used in combination with the developed K_{TC} concept to predict THM concentrations after two-hours for each of the different test conditions. In general, predicted concentrations were usually within ± 5 µg/l TTHM (average of ± 3.9 µg/l, or 13.8 %) of the observed concentrations (for Stensham WTW tests alone), and ± 5 µg/l TTHM (average of ± 3.4 µg/l, or 11.8 %) of the observed concentrations across the six WTWs.
- TOC removal varied through the WTW, with an average removal of 55 % of raw water TOC concentrations being removed by the final water. The clarification process accounted for the majority (60-80 %) of this decline.
- Successive treatment processes through Strensham WTW led to a reduction in the water's reactivity in terms of chlorine decay and THM formation. Bulk decay constants declined from an average of 1.73 l/hr at the raw water to 0.15 l/hr at the post-GAC sampling point (over 2-hours). There were successive declines of 20 %, 9 % and 16 % in the amount of THM formed following the clarification, filtration and GAC unit processes, respectively,

indicating the removal of potential THM precursor material with each subsequent treatment process.

- A simple, yet robust, approach to the modelling of chlorine decay and THM formation has been developed, through the use of derived chlorine decay constants and K_{TC} values. Promising results have been obtained, with predicted data reflecting measured data.

8.1.2 Conclusions with respect to objectives

Objective 1: To undertake a detailed analysis and cross comparison of THM formation and chlorine decay in six water supply systems, relating the differences to WTW operational and source water characteristics, supply procedures, and temporal and spatial variation in each of the foregoing, in order to try and understand critical factors in each of the six systems.

A significant amount of field and laboratory work has been undertaken in this study to investigate THM formation and chlorine decay in six WTWs and part of their associated distribution systems. Due principally to cost and time constraints, Strensham WTW was chosen to be investigated in depth.

Of the six WTW studied, Strensham WTW is the only one to be fed directly from a river source (R. Severn), and thus is the most susceptible to a greater fluctuations in raw water quality. The distribution system is well defined with long stretches solely fed by Strensham water, with well-understood hydraulics, making it an apposite choice as the most studied

WTW. Some of the key findings from this work, with respect to Strensham WTW and the remaining five WTWs, respectively, are:

- **Strensham WTW and distribution system results**

- Bromide raw water quality is low flow critical as it varies inversely with river flow due to a combination of run-off dilution of urban inputs from STW effluent and CSO, and, of groundwater inputs.
- TOC raw water quality is high flow critical as it varies with river flow, principally due to catchment run-off transport effects and characteristics.
- TOC removal varied through the WTW, with an average removal of 55 % of raw water TOC concentrations being removed by the final water. The clarification process accounted for the majority (60-80 %) of this decline. TOC removal across the WTW was shown to be related to coagulant dose, with an approximate 10 % reduction in TOC concentrations per 1 mg/l increase in the coagulant dose.
- A five-year data set showed final water THM concentrations to be correlated with final water TOC and temperature. Little bromide data was available at this point. Unexplained variance led to the requirement for controlled experiments, conducted under both ambient and laboratory conditions, designed to simulate operational conditions.
- Final water THM speciation correlated with raw water TOC and raw water bromide concentrations due to raw water quality variations and the shifting carbon : chlorine : bromide ratios in the contact tank.

- **Inter-comparison of 6 WTW and parts of their distribution systems**

- Each of the selected water supply systems had a history of high THM concentrations with recent strategies for reduction, due to the increasing concerns with respect to regulatory standards and health concerns.
- Data for the summers of 2007 and 2008 showed the complexity of factors affecting the THM concentrations by the time water arrived at the end of distribution systems. A quantitative analysis based on subjectively defined high, medium and low risks with respect to THM formation found that (Table 4.5):
    - High raw water bromide and TOC concentrations affected two and three WTWs, respectively.
    - High final water TOC concentrations affected one WTW.
    - High contact tank inlet and outlet concentrations affected two WTWs.
    - High final water THM concentrations affected two WTWs.
    - Long (> 90 hours) travel times affected three distribution systems.
    - High free chlorine concentrations (≥ 0.4 mg/l) affected four of the distribution systems.
    - The percentage of THM concentration formed in the WTW varied between 40 and 65 % of the final customer tap value.
    - For final customer tap THM concentrations of 40 – 60 μg/l, the systems has between 0 – 6 critical factors.
- Given the complexity of influences leading to final tap THM concentrations, modelling was highly desirable to aid efficient management of THM concentrations.

Objective 2: To investigate the influence of water quality parameters, initial chlorine concentration, temperature, contact time, water treatment unit and supply processes on chlorine decay, in order to develop empirically based models to relate functional dependencies to each other.

A number of significant findings on the decay of chlorine have emerged from this study, which increase the understanding of the mechanisms of chlorine decay through WTW and distribution systems, specifically under conditions of no pre-chlorination at the WTW:

- **Strensham WTW and distribution system results**

  - Successive treatment processes through Strensham WTW led to a reduction in the waters reactivity with bulk decay constants falling from an average of 1.73 l/hr at the raw water to 0.15 l/hr at the post-GAC sampling point (over 2-hours) (Figure 5.6). The main reduction occurred due to the clarification process, with an average percentage decline of approximately 75 % in inlet decay constants.
  - A first order model, although sufficient for an initial comparison of different waters' reactivities, was shown to be inappropriate for modelling chlorine decay in a contact tank, due primarily to the rapid reactions that occur in the early stages upon the first chlorination.
  - With the omission of the first 5-minute period of the chlorine decay test, the average R^2 value of fitted ln-linear trend lines increased from 0.69 to 0.91. Further extensions to the initial period of the tests were shown to not significantly improve accuracy.

- A two stage modelling process was proposed, where the initial 5-minute period of chlorine decay would be represented by a percentage drop in C_0 (calculated by applying a factor, *p*, to C_0), followed by first order modelling of the latter stage. This was deemed for predictive purposes to be suitable for contact tank time scales of the order of an hour.
- Application of the two stage process to the range of test conditions showed encouraging results with concentrations approximately ± 0.05 mg/l (± 4.2 %) from the observed concentrations after 60 minutes and ± 0.1 mg/l (± 6.5 %) after 120 minutes.
- The first order bulk decay constant (K_B) was observed to vary with the initial chlorine concentration (C_0), TOC, bromide and temperature, to which K_B;
    - had an inverse relationship with C_0 and bromide;
    - had a positive power relationship with TOC;
    - had a positive relationship with temperature, where a two-fold increase in K_B was observed with the rise in temperature from 5 ^oC to 25 ^oC.
- First order decay approximations were found to be more appropriate to model chlorine decay in the distribution system, with R^2 values for the fitted ln-linear trend lines ranging between 0.90 and 0.99, averaging 0.95. Average bulk decay constants fall by approximately 50 % from 0.051 l/hr at the final water to 0.027 l/hr immediately after the first re-chlorination at the outlet to Oversley Green BPS outlet. Bulk decay constants continue to decline through the distribution system, although at a diminishing rate.
- As the final water and distribution system tests were conducted at a range of ambient conditions it is difficult to discern any palpable relationships between bulk decay constants and individual water quality parameters. However, a positive linear

relationship of the bulk decay constant with temperature is evident at the final water (R^2 ~ 0.69), Oversley Green BPS outlet (R^2 ~ 0.80) and at Tysoe DSR outlet (R^2 ~ 0.81). A doubling of temperature from 10 ^{o}C to 20 ^{o}C leads approximately to a 50 % increase in the bulk decay constants at these points.

- **Inter-comparison of 6 WTW and parts of their distribution systems**

- Raw water bulk decay constants over 2-hours ranged between 0.7 and 1.46 l/hr (average ~ 1.12 l/hr) across the six WTWs, with the most reactive waters present at sites where raw water storage is small or non-existent, *e.g.* Whitacre, Campion Hills and Strensham WTWs.
- As at Strensham WTW, an inverse relationship was observed between initial chlorine concentration and bulk decay constants was again observed on most of the sampling days at each of the WTWs, with the average bulk decay constants (between 5-60 minutes) decreasing by 35% and 20 %, between 1.3 – 1.7 mg/l and 1.7 – 2.1 mg/l respectively. Similarly, for bulk decay constants between 5-120 minutes there was an increase of 28 % and 23 % over the same changes in chlorine concentration. Temperature can be seen to have a significant positive relationship, with the average bulk decay constants across the six WTWs (between 5-60 minutes) increasing by 24 % and 58 %, between 5 ºC – 15 ºC and 15 ºC – 25 ºC respectively. Similarly between 5-120 minutes there was an increase of 36 % and 53 % over the same changes in temperature. Predictably, bulk decay constants at each of the six WTWs are seen to decrease by approximately a factor of two with the dilution of the sample water from 1:0 to 2:1 and from 2:1 to 1:2 (sample water {SW} : distilled water {DW}).

- K_B (one and two hour values) variation with TOC and bromide could be represented by linear variations, although with a poorer fit for a specific WTW. This indicates that global functions could be used for initial modelling of these, and similar WTW, without the need for costly WTW specific model calibration data.
- Correlation between predicted and observed free chlorine concentrations using the adopted two stage approach at each of the six WTWs was found satisfactory, although the relationship weakened with time. The average difference between observed and predicted chlorine concentrations across the six WTWs decreased from 0.039 mg/l (2.9 %) after five minutes, to 0.047 mg/l (4.1 %) after one-hour, and 0.061 mg/l (6.7 %) after two-hours.

Objective 3: To investigate THM formation in relation to key water quality parameters, initial chlorine concentration, temperature, contact time and water treatment unit and supply processes, and consequently to determine appropriate THM formation models.

The formation of THM in water was found to be inherently complicated and affected by a large number of parameters, of which chorine dosage, organic content, temperature, bromide concentration and contact time were highlighted as being of particular significance. Based on the combination of field and laboratory determinations, the following main conclusions were obtained:

- Laboratory data showed that successive treatment processes at Strensham WTW removed cumulative amounts of THM precursor material, resulting in a decline in

TTHM formation during two-hour tests conducted on water through the WTW at similar test conditions (Figure 6.1). The average TTHM concentration formed fell from 33.3 µg/l average at raw water to 18.3 µg/l at the post-GAC sampling point. The greatest reduction occurred across the clarification process (where a 6.8 µg/l difference was observed between average raw and post-clarifier samples).

- A propensity to remove organic matter with little change in bromide led to a shift from chloroform as the predominant THM specie at the inlet of Strensham WTW (78 %) to an increase in the percentage share of brominated species (with chloroform only accounting for 38 % of TTHM by post-GAC samples). Corresponding BIFs also reflected this, increasing from 0.28 at the raw water to 1.10 at the post-GAC stage.
- Mirroring the decay of chlorine, the rate of THM formation was initially rapid, followed by a declining rate (approximately 43 % of the total amount of THM formed over two-hours occurs within the initial five-minutes of the start of the test) (Figures 6.12 and 6.13).
- Bromide conversion was also greatest in the early stages of these tests, with 36 % (21.1 µg/l) and 51 % (22.8 µg/l) drops in the initial bromide concentrations on the 1st and 2nd sampling days half way through the 4-hour tests.
- THM formation was shown to increase with contact time, C_0, temperature, TOC, and bromide concentrations. Bromide was negatively, and TOC positively, linked with a higher fraction of chloroform as a percentage of TTHM species and lower BIF. The decline in bromide conversion over the two-hour bulk decay tests was greater with higher C_0 and temperatures.
- THM formation was found to be higher in the summer months than spring months for similar TOC and bromide concentrations in the water, indicating a different,

potentially more reactive chemical matrix of the water in the summer months, a concern when considering other seasonal factors such as temperature being higher in the summer months.

- The use of K_{TC} values (the amount of unit THM produced per unit chlorine consumed) was shown to be an expedient basis for modelling THM formation in operational circumstances.
- All post-GAC water tests, with the omission of sample water dilution tests, which showed unpredictably high THM concentrations, yielded an average K_{TC} value of 34 µg/l TTHM per mg/l free Cl.
- All the data from post-GAC tests was collated using SPSS (via stepwise regression) to develop an equation for calculating K_{TC} values of the form:

$$K_{TC} = A + (a \cdot C_0) + (b \cdot \Theta) + (c \cdot TOC) + (d \cdot Br) \qquad (6.3)$$

- This equation was used in combination with the chlorine modelling equations developed in Chapter 5 to calculate THM concentrations after two-hours for each of the different test conditions. In general, THM concentrations were slightly over-predicted, although the predicted concentrations were usually within ± 5 µg/l TTHM (average of ± 3.9 µg/l, or 13.8 %) of the observed concentrations (for Stensham WTW tests alone), and ± 5 µg/l TTHM (average of ± 3.4 µg/l, or 11.8 %) of the observed concentrations across the six WTWs.
- K_{TC} values were shown not to have a statistical dependence on temperature, there was a weak dependence on chlorine, TOC and bromide (to a level of 15 % significance*)*. A

probable explanation for this is the complicated effect of varying bromide : chlorine, bromide : TOC, and chlorine : TOC ratios.

Objective 4: To consolidate the analysis into a cost-effective, spreadsheet model that can be practically applied in operational circumstances, enabling the user to enter prevailing water quality and WTW operational characteristics to predict chlorine use and THM formation from source water to customer tap.

- A simple, yet robust, approach to the modelling of chlorine decay and THM formation has been developed, through the use of derived chlorine decay constants and K_{TC} values for various types of waters under a range of operational conditions.
- Despite not offering a robust interpretation of the complex relationship between TOC and bromide with bulk decay and THM formation, the model has been shown to be fit for purpose for one of the six studied WTWs (Strensham WTW).
- Promising results have been obtained, with predicted data reflecting measured data. Although some over-prediction of both processes has been found in the contact tank, results in the distribution system are more encouraging, with concentrations at the extremities being within 6 µg/l of the observed concentrations on a sampling day with similar ambient conditions to reference values applied (Figure 7.1).

Objective 5: To apply and critically evaluate the proposed model for one of the supply systems studied, thus identifying mitigation strategies for the management of THMs.

- Relying only on the measurement of analytically undemanding parameters (in particular, chlorine and its decay with time), under appropriate circumstances the model developed offers advantages of simplicity and cost-effectiveness over other, more complex models. The model can thus be applied to assess the chemical risk under different scenarios allowing for informed decision making.
- Strategies in controlling chlorine decay and THM formation have been suggested and potential water quality and operational scenarios applied through the model.
- TOC and temperature were shown to be the most significant factors in determining TTHM concentrations in a relatively low bromide water supply system. Although temperature is an unmanageable external factor, organics removal through the WTW was shown to significantly impact the downstream concentrations of THM formed.

8.2 Future work

- There is still some unexplained variance in the data analyses that could benefit from further investigation at specific WTWs.
- The model has only been applied to one system and it needs to be critically assessed for other systems, particularly those with higher bromide concentrations where model function modifications will probably be necessary.
- The current form of the model takes a deterministic approach. With a modest supplementation of the data the model could be extended to give predictions in a stochastic form which is more appropriate for risk assessment.
- The addition of the prediction of microbiological risk should be considered given the availability of suitable data.

- The current model has not considered pH variations, which are a common method of changing coagulation efficiency. Further laboratory and WTW investigation would be necessary to enable this feature to be incorporated.
- Raw water quality has been shown to be related to river flow characteristics thus opening up the possibility of linking drinking water quality models to flow forecasting systems.
- The present study has shown similarities in the resultant relationships between UV_{254} absorbance and TOC with chlorine decay and THM formation. Since the measurement of UV_{254} absorbance is relatively easy to measure it would be of practical significance if one can clarify the conditions under which UV_{254} absorbance can be used as a surrogate parameter for TOC.
- For simplicity first order rate equations have been used wherever possible. More refined approaches could be considered, providing justification is given for an increased complexity and cost in their application.
- Water quality regulation is increasingly considering specific THM species. This work has demonstrated trends in THM speciation affected by several factors. These could be investigated and incorporated in the model. Additionally, this study concentrated explicitly on THMs, which are only one group of several hundred currently identified DBPs. The prospect of future regulation, resulting from improved epidemiological evidence and understanding, will require future investigation over a wider range of DBP categories.

Appendix A Alternative Disinfectants

A.1 Ozone

Ozone is the strongest oxidant of the common disinfecting agents. Ozone was discovered in 1783 by Van Marum, and named by Schonbein in 1840. In 1857, the first electric discharge ozone generation device was constructed by Siemens, with the first commercial application of this device occurring in 1893 (Haas, 1999).

Ozone is highly toxic, corrosive and, in it’s purest form, explosive. In drinking water treatment it is used at concentrations of 2-6 % depending on the production process (STW Design Manual, 2006). Ozone is used in a similar manner to chlorine. However, due to it’s high instability it can not be transported and must be generated at the point of use.

Ozone is produced, not as a chemical but as a pure mixture with air. It is produced using a method called the Corona discharge method, which involves passing dry-oxygen bearing gas through a gap with a low current electrical discharge (Karnik *et al*, 2005).

Ozone reacts rapidly at first with inorganic compounds like iron and manganese, then with organics and finally as a disinfectant. In clarified waters, typical contact time for disinfection is 0.4 mg/l for 4 minutes, or a *Ct* value of 1-2 mg/min/l. Since ozone is highly toxic, the off-gas has to pass through an ozone destructor, either thermal (350-370°C) or catalytic (using manganese, palladium or nickel oxide based catalyst) (Severn Trent Design Manual, 2006).

Ozone, being a strong oxidizing agent, reacts directly with constituents found in solution and is also capable of forming highly reactive chemical agents, such as hydrolxyl radicals and organic radicals which, along with aiding the decomposition of ozone, are responsible for non-selective (compared to the direct ozone reaction) oxidation of a variety of organic materials (Guay *et al*., 2005).

Apart from the obvious benefit of being a more effective disinfectant than chlorine, ozone, being such a powerful oxidant, has additional advantages. It is effective in reducing colours and odours, improving suspended solids removal, conditioning sludges and oxidising pesticides and herbicides (Masten *et al*, 1994, Karnik *et al*, 2005, ST Design Manual, 2006).

Ozone can be added at various points within the water treatment process depending on the intended application (Figure A.1). Like chlorination, ozonation also forms a residual, however due to it's short life span it is negligible for preventive measures in distribution systems, and is therefore usually used in conjunction with a disinfectant capable of providing a residual adequate for the distribution system fed.

The use of ozonation in water treatment processes results in a decrease in the formation of THMs and haloacetic acids upon subsequent chlorination (Richardson *et al*., 1999). Increases in ozone dosages have been shown to result in a corresponding decrease in the concentrations of THMs and HAAs formed from subsequent chlorination (Amy *et al*., 1988; Cipparone *et al*., 1997; Karnik *et al*, 2005). The reactions that occur during ozonation produce by-products, including aldehydes (formaldehyde, glyoxal, and methylglyoxal), ketones, glyloxylic acid and pyruvic acid (Richardson, 2003; Guay *et al*., 2005). Some of these by-products are of concern due to their mutagenicity and carcinogenicity (Bull *et al*., 1984; Richardson, 2003; Richardson *et al*., 2007). Also as these products are easily biodegradable, they can serve as substrates for microbial re-growth in the distribution system (Karnik *et al*., 2005). They can however be removed by bio-filtration, as work by Karnik *et al*. (2005) showed. In their research, a combination of ozonation and membrane filtration was used prior to chlorination. Results showed the formation of partially oxidized compounds from NOM that were less reactive with chlorine, and subsequently decreased the concentration of simulated distribution system total THMs and simulated distribution system haloacetic acids by up to 80 % and 65 %, respectively.

Other major disadvantages of ozone are the high capital and operational costs and that it requires skilled staff in order to operate and maintain an ozone plant. Ozone also gives rise to the formation of bromates (a regulated substance) when bromide is present in the water (Miltner *et al*., 1992; Richardson *et al*., 1999; Freese *et al*., 2004). Ozonation is practised at one of the six water treatment works under investigation in this study (Campion Hills WTW).

A.2 Ultraviolet (UV)

The highly effective germicidal properties of ultraviolet light have been known for more than 100 years. The first full scale use of UV for wastewater disinfection was in 1910 (Haas, 1999). The use of UV light became more widespread with the invention of neon tubes in 1940s, which introduced the low pressure mercury vapour lamp, providing a practical and economic source of UV light for the first time (USEPA, 1996). By the early 1980's, UV disinfection for wastewater had gained popularity due in part to the more stringent regulatory requirements affecting the use of chlorine within the wastewater treatment process and subsequent discharge. Whilst use in drinking water treatment is not as widespread, its use is gaining in popularity due to a number of benefits it has over chemical disinfectants, one prominent example, being virtually no production of harmful by-products.

UV light is high energy light, with a wavelength too short for the human eye to see. For UV light to work, the UV rays must actually come into contact with the cell wall. Studies have shown that when the light penetrates the cell wall, UV rays are absorbed up to a point when the cell's DNA is modified, preventing infection (Eccleston, 1998). Ultraviolet disinfection works best for germicidal purposes at a range of between 250 – 270 nm (STW Design Manual, 2006), for a specified time period at the specified intensity.

UV disinfection has numerous other advantages over alternative disinfectants (primarily because it is not of a chemical form):

- UV disinfection has no known toxic, or significant non-toxic by-products (National Drinking Water Clearinghouse, 2000);
- UV treatment does not alter the water in anyway chemically; nothing is being added except energy. Therefore, there is no danger of overdosing, there is no on-site smell and no smell in the final water product, it does not require storage or handling of hazardous materials;
- It requires very little contact time (seconds versus minutes for chemical disinfection);
- It removes some organic contaminants and has no volatile organic compound (VOC) emissions or toxic air emissions.
- No known formation of disinfection by-products (eg. THMs, HAAs, aldehydes, bromate, ketoacids).

Under ideal conditions, UV disinfection is known to kill 99 % of bacteria in drinking water treatment (Hass, 1999). Even with this performance UV disinfection has some limitations;

- UV units only kill bacteria at one point within the system and as such does not add a residual germicidal effect downstream. This means it only takes one bacteria to pass through unharmed, leaving the chance of it attaching itself on a pipe downstream and proliferating;
- Certain contaminants in water can reduce the transmission of UV light, restraining the UV dose that reaches the bacteria. These UV absorbing contaminants include turbidity, iron, and humic and fulvic acids (Qualls *et al*., 1985). UV disinfection is therefore not suitable for water with high levels of suspended solids, turbidity, colour or soluble organic matter;

- All UV units have a maximum flow-rate capacity and some also have a minimum flow-rate. If the flow is too high, water will pass through without enough exposure. If the flow rate is too low, heat may build up, causing damage to the UV lamp (Eccleston, 1998);
- Bacteria cells are not removed in a UV unit but are converted to pyrogens. The killed micro-organisms and any other contaminant in the water are a food source for any bacteria that do survive downstream (Edstrom Industries, 2003).

Due to the above limitations, UV disinfection is predominantly used in smaller treatment plants for waters typically from groundwater sources.

A.3 Chloramine / Monochloramine

Chloramine, or monochloramine, is the product of the reaction between chlorine and ammonia. Free chlorine is converted to chloramine, the reaction is pH, temperature and chlorine to ammoniacal nitrogen ratio dependant (Roberts, 2004). Its disinfecting power is less efficient, with exposure times between 25 to 100 times longer compared to its free chlorine equivalent (Stevens *et al.*, 1989).

The ammoniacal nitrogen will react to successively form mono, di and tri-chloramines (more commonly known as nitrogen tri-chloride) (described by equations 2.13, 2.14 and 2.15 respectively).

Unlike chlorine, chloramines do not combine with organics in the water to form potentially dangerous THMs. However other DBPs, most of which have received not as much research as

THMs, may be formed. The formation of halojetones, chloropicrin, cyanogen chloride, haloacetic acids, haloacetonitriles, aldehydes and chlorophenols have all been reported from its use (Krasner *et al*., 1989; Bull & Kopfler, 1991; Freese *et al*., 2004).

By switching from chlorination to a chloramine process, the tap water may have more colour. Colour comes from natural organics in the water (*e.g*. tannins, humics) derived from decayed plant matter. Because the chlorine is no longer reacting with and consuming organics, a greater amount of colour may therefore remain in the tap water.

Monochloramine is generally not used as a primary disinfectant as it is weak in the inactivation of viruses and protozoa. However, because of its persistence, it is an attractive secondary disinfectant for maintenance of a stable disinfectant residual in the distribution system. However, care must be taken in selecting the proper ammonia-to-chlorine ratio so that nitrification problems do not occur in the distribution system (Singer, 1994; Carlson & Hardy, 1998).

In general, it is considered inadvisable to mix chloraminated water and water disinfected with free chlorine in a distribution system. At the zone where the two different waters interact, the free chlorine can chemically react with the monochloramine, reducing the available free chlorine residual and forming dichloramine or nitrogen trichloride. Monochloramine is the preferred chloramines species for use in water treatment because it causes less taste and odour problems compared to the other chloramines species.

A.4 Chlorine dioxide

Chlorine dioxide was first produced from the reaction of potassium chlorate and hydrochloric acid by Davy in 1811 (Miller, 1978). However, it was not until the industrial scale preparation of sodium chlorite, from which chlorine dioxide may more readily be generated, did its widespread use occur.

Chlorine dioxide is used as a gas, and as a result is harder to control in the water treatment plant environment. It is never stored on site, but is produced as a solution on site, usually reacting sodium chlorite with hyrdrochloric acid or chlorine. It is more volatile than the other disinfectants but at the same time is relatively stable (Haas, 1999; Hua, 1999). The disinfection process is more efficient than free chlorine but its volatile nature keeps it from being a widely used alternative.

The reaction of chlorine dioxide with material present in waters containing chlorine dioxide demand appears to be less significant than in the case with chlorine (Hass, 1999). Rather, the dominant cause of loss of chlorine dioxide during disinfection may be the direct reactions with water and inter-conversions to chlorite, chlorate, and chloride, which are regulated contaminants like other DBPs. Chlorine dioxide is a more effective disinfectant and oxidant than chlorine. Unlike chlorine, it does not cause the disagreeable odour and, in general, chlorine dioxide itself has been found to produce fewer organic by-products with naturally occurring organic material, although some non-purge-able organic halogenated are formed (Rav-Acha, 1984).

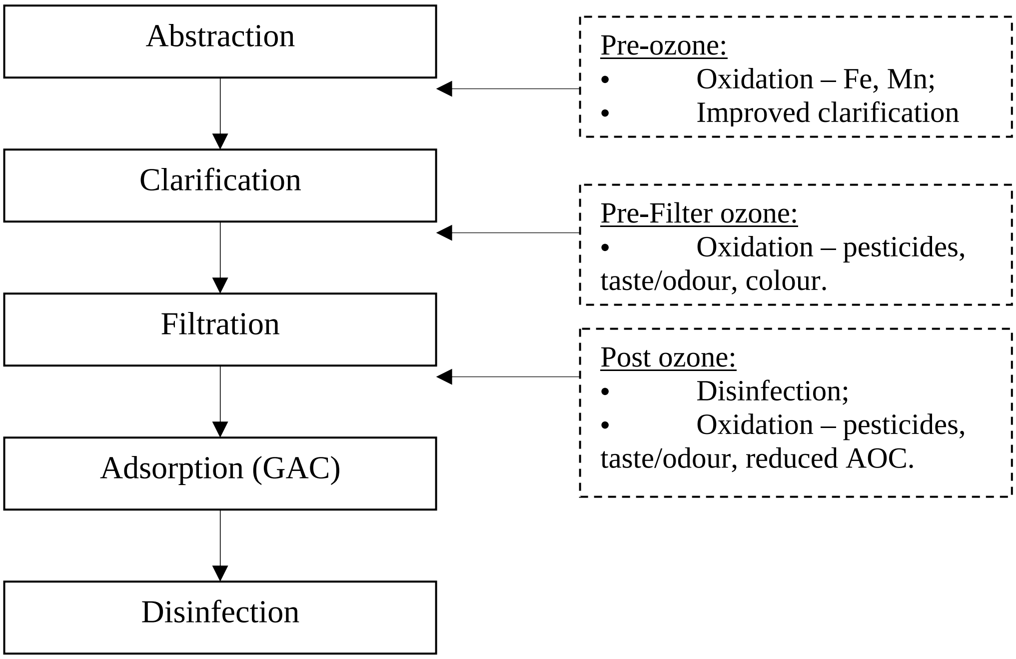


Figure A.1; Application points and reasons for ozone appliance.

Appendix B THM Epidemiological Studies

Epidemiological evaluation of chlorination by-products in drinking water commenced soon after chloroform was discovered in 1974 in drinking water supplies and has continued to the present day (IARC, 1976, 1991; Fawell, 2000; Moudgai *et al*., 2000; Villanueva *et al*., 2004; McDonald & Komulainen, 2005; WHO, 2005; Bove *et al*., 2007; Wang *et al*., 2007). Some of the initial studies used geographic comparisons of water source and localized cancer mortality rates (Bull et al., 1995), but due to the extensive number of uncontrollable external factors the relationships formed have often been unreliable and fraught with inaccuracies. As a result, reliance has been placed on controlled epidemiological and toxicology studies on laboratory animals.

From these studies, association between the ingestion of chlorinated drinking water (in excess) with risk of cancer, particularly of bladder and rectal, have been reported (IARC, 1991; Morris *et al*., 1992; Cantor, 1994; WHO, 2005; Bove *et al*., 2007). More recently the emphasis has shifted from cancer to reproductive effects, such as intrauterine growth retardation, low birth weight, preterm birth, congenital malformations, and stillbirth (Nieuwenhuijsen *et al.*, 2000; Graves *et al.*, 2001; Villanueva *et al*., 2007).

Tables 2.3 and 2.4 detail the classifications of the four main THM species as of January 1999. USEPA (1999) reported that of the four THMs, chloroform, bromodichloromethane and bromoform are type B2 (probable human carcinogens) and chlorodibromomethane is type C (possible human carcinogen).

Humans are also exposed to mixtures of DBPs, rather than individual DBPs, therefore the majority of currently available single chemical studies in experimental animals will not represent the true effects of everyday exposure to DBPs and scaled representative analysis is inherently complicated.

Furthermore, traditional risk assessments for drinking water often are restricted to ingestion of exposure to toxic chemicals. However, drinking water is also used, for example, in cooking, washing, bathing, laundering and cleaning, therefore ingestion is only one exposure pathway of many. Studies on the relative importance of these pathways indicate that exposure to toxic chemicals, such as THMs, through routes other than direct ingestion may be as large as, or larger than ingestion alone (Lee et al., 2004; Jo *et al*., 2005; Wang *et al*., 2007).

Despite rigorous scientific research studies, no conclusive evidence has ever been found to prove that THMs, in the quantities in which they occur in drinking water, are harmful to humans. Based on the numerous studies conducted on laboratory animals, the margin of exposure for humans from the highest chloroform dose that produced no adverse effect, is estimated to be between 34,500 and 43,000 mg/kg per day (Freese *et al*, 2004). The margin of exposure is the difference in the concentration in tap water of the compound that produces no development toxicity (Tardiff *et al*, 1999). An average adult man, weighing between 70 and 90 kg, would have to drink 8 glasses of water a day (around 1.5 l) containing between 1500 and 2000 mg/l chloroform in order to ingest a dose the size of this margin of exposure (Freese *et al*, 2004). The fact that levels of THMs normally found in water are in microgram quantities, many orders of magnitude lower than 1,500 to 2000 mg/l, indicates the unlikely threat posed by this THM to human health from potable water supplies.

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