CRANFIELD UNIVERSITY

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# Haloacetic Acids and other Disinfection By-Products in UK Treated Waters: Occurrence, Formation and Precursor Investigation

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Centre for Water Science

PhD

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# ABSTRACT

Disinfection by-products (DBPs) in drinking water are formed when natural organic matter (NOM) that remains after initial treatment reacts with disinfectants, such as chlorine or chloramines. DBPs, which are of health concern, can take the form of trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloacetaldehydes (HAs), halonitromethanes (HNMs) and a host of other halogenated DBPs. So far, regulations in the United Kingdom (UK) only encompass the group of THMs allowing a maximum level of 100 µg/L. HAAs, the second most prevalent class of DBPs, are currently under consideration by the European Union to be regulated at 80 µg/L.

Reliable and reproducible quantification methods are required for DBP detection. To address this need, the presented work includes a comparative study between analytical devices, which concludes that GC/ECD is the only approach with suitable detection limits. This work reports an investigation of the DBP formation potential (FP) of waters from 11 water treatment works (WTWs) at different locations in the UK. Several of these waters have shown to form significant levels of HAAs and THMs. Furthermore, other DBPs, such as iodo-THMs (i-THMs), HANs, HKs, HAs and HNMs were detected. It has also been confirmed that improving the control of these DBPs can be achieved by using monochloramine instead of free chlorine. A statistical analysis revealed that THMs correlated well with the HAAs, and as a result the regulatory limit of 100 µg/L for the $THM_4$ would fail a regulation of 80 µg/L for the nine HAAs.

A number of parameters have been identified, which have particular relevance when considering the formation of HAAs and THMs in treated waters. Threshold bromide level was determined beyond which speciation of DBPs shift toward brominated species. The pH, which significantly affected THMs, was less strongly linked to the HAAs. The temperature had a consistent impact with a decreasing DBP formation at lower temperatures. Increasing the contact time with the disinfectant resulted in parallel first order reaction kinetics of the HAAs and THMs. Finally, the precursors involved in the formation of DBPs were found to be specific to water sources.

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# ABBREVIATIONS, CHEMICAL FORMULA AND NOTATION

## Abbreviations and Chemical Formula

| | | |
|---|---|---|
| 1,1-DCP | 1,1- dichloropropanone | |
| 1,1,1-TCP | 1,1,1- trichloropropanone | |
| | | |
| amu | Atomic Mass Unit | |
| APHA | American Public Health Association | |
| ASG | Anthracite, Sand and Garnet | |
| AWWA | American Water Works Association | |
| AwwaRF | Awwa Research Foundation | |
| | | |
| BCAA | Bromochloroacetic Acid | (µg/l) |
| BCAN | Bromochloroacetonitrile | (µg/l) |
| BCIM | Bromochloroiodomethane | (µg/l) |
| BDCAA | Bromodichloroacetic Acid | (µg/l) |
| BDCM | Bromodichloromethane | (µg/l) |
| BDIM | Bromodiiodomethane | (µg/l) |
| BIF | Bromine Incorporation Factor | |
| $Br^-$ | Bromide Ion | |
| | | |
| CDIM | Chlorodiiodomethane | (µg/l) |
| CE | Capillary Electrophoresis | |
| $CH_3CN$ | Acetonitrile | |
| CHO | Chinese Hamster Ovary | |
| $Cl^-$ | Chloride Ion | |
| $Cl_2$ | Chlorine | |
| $CO_2$ | Carbon Dioxide | |
| CZE | Capillary Zone Electrophoresis | |
| | | |
| D/DBPR | Disinfectants/Disinfection by-Product Rule | |
| DAF | Dissolved Air Flotation | |

| | | |
|---|---|---|
| DBAA | Dibromoacetic Acid | (µg/l) |
| DBAN | Dibromoacetonitrile | (µg/l) |
| DBCAA | Dibromochloroacetic Acid | (µg/l) |
| DBCM | Dibromochloromethane | (µg/l) |
| DBIM | Dibromoiodomethane | (µg/l) |
| DBNM | Dibromonitromethane | (µg/l) |
| DBP | Disinfection By-Product | (µg/l) |
| DBP-FP | Disinfection By-Product Formation Potential | |
| DCA | Dichloroacetaldehyde | (µg/l) |
| DCAA | Dichloroacetic Acid | (µg/l) |
| DCAN | Dichloroacetonitrile | (µg/l) |
| DCBM | Dichlorobromomethane | (µg/l) |
| DCIM | Dichloroiodomethane | (µg/l) |
| DNA | Deoxyribonucleic Acid | |
| DOC | Dissolved Organic Carbon | (mg/L) |
| DON | Dissolved Organic Nitrogen | (mg/L) |
| DVB | Divinyl Benzene | |
| DWI | Drinking Water Inspectorate | |
| DXAA | Dihalogenated Acetic Acid | (µg/l) |
| | | |
| ED | Electrochemical Detector | |
| EI | Electron Ionisation | |
| EOM | Extracellular Organic Matter | |
| EPA | Environmental Protection Agency | |
| ESI/MS | Electrospray Ionization/ Mass Spectrometry | |
| | | |
| FP | Formation Potential | |
| | | |
| GAC | Granular Activated Carbon | |
| GC | Gas Chromatography | |
| GC/ECD | Gas Chromatography/Electron Capture Detector | |
| GC/MS | Gas Chromatography/Mass Spectrometry | |
| GC/TOFMS | Gas Chromatography/Time of Flight Mass Spectrometry | |

| | | |
|---|---|---|
| $H^+$ | Hydrogen Ion | |
| $H_2CO_3$ | Carbonic Acid | |
| $H_2SO_4$ | Sulphuric Acid | |
| $H_3O^+$ | Hydronium Ion | |
| HA | Haloaldehyde | (µg/l) |
| HAA | Haloacetic Acid | (µg/l) |
| $HAA_3$ | Sum of three HAAs | (µg/l) |
| $HAA_5$ | Sum of five HAAs | (µg/l) |
| $HAA_6$ | Sum of six HAAs | (µg/l) |
| $HAA_9$ | Sum of nine HAAs | (µg/l) |
| HAA-FP | Haloacetic Acid Formation Potential | |
| HAN | Haloacetonitrile | (µg/l) |
| HCl | Hydrogen Chloride | |
| HK | Haloketone | (µg/l) |
| HOBr/$OBr^-$ | Hypobromous Acid/Hypobromite Ion | |
| HOCl/$OCl^-$ | Hypochlorous Acid/Hypochlorite Ion | |
| HOI | Hypoiodous Acid | |
| HPI-A + N | Hydrophilic Acid + Neutral | |
| HPI-B | Hydrophilic Base | |
| HPI-N | Hydrophilic Neutral | |
| HPLC | High Performance Liquid Chromatography | |
| HPO-A | Hydrophobic Acid | |
| HPO-B | Hydrophobic Base | |
| HPO-N | Hydrophobic Neutral | |
| HPSEC | High Performance Size Exclusion Chromatography | |
| Hz | Hertz | |
| | | |
| IC | Ion Chromatography | |
| ICP/MS | Inductively Coupled Plasma/Mass Spectrometry | |
| $IO_3^-$ | Iodate | |
| IS | Internal Standard | |
| i-THM | Iodo-THM | |

| | | |
|---|---|---|
| $KH_2PO_4$ | Potassium Acid Phosphate | |
| LLE | Liquid-Liquid Extraction | |
| LOD | Limit of Detection | |
| m/z | Mass to charge ratio | |
| MBAA | Monobromoacetic Acid | (µg/l) |
| MCAA | Monochloroacetic Acid | (µg/l) |
| MCL | Maximum Contaminant Level | |
| MRL | Maximum Reporting Level | |
| MtBE | Methyl tert Butyl Ether | |
| MW | Molecular Weight | |
| MX | 3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone | |
| MXAA | Monohalogenated Acetic Acid | (µg/l) |
| $NaHCO_3$ | Sodium Bicarbonate | |
| NaOCl | Sodium Hypochlorite | |
| $Na_2CO_3$ | Sodium Carbonate | |
| $Na_2HPO_4$ | Phosphate Dibasic | |
| $Na_2SO_4$ | Sodium Sulphate | |
| NCI | National Cancer Institute | |
| $NCl_3$ | Trichloramine | |
| NDMA | N-nitrosodimethylamine | |
| $NHCl_2$ | Dichloramine | |
| $NH_2Cl$ | Monochloramine | |
| $NH_3$ | Ammonia | |
| $NH_4Cl$ | Ammonium Chloride | |
| $NH_4OH$ | Ammonium Hydroxyde | |
| NOM | Natural Organic Matter | |
| NPOC | Non Purgeable Organic Carbon | (mg/L) |
| pH | potential Hydrogen | |
| PHB | Polyhydroxybutyrate | |

| | | |
|---|---|---|
| P&T | Purge and Trap | |
| PTFE | Polytetrafluoroethylene | |
| RSD | Relative Standard Deviation | |
| SPE | Solid Phase Extraction | |
| SUVA | Specific Ultraviolet Absorbance | (L/m-mg C) |
| $SUVA_{254}$ | Specific Ultraviolet absorbance at 254 nm | (L/m-mg C) |
| SV | Semi-Volatile | |
| TBAA | Tribromoacetic Acid | (µg/l) |
| TBM | Tribromomethane | (µg/l) |
| TC | Total Carbon | |
| TCA | Trichloroacetaldehyde | (µg/l) |
| TCAA | Trichloroacetic Acid | (µg/l) |
| TCAN | Trichloroacetonitrile | (µg/l) |
| TCM | Trichloromethane | (µg/l) |
| TCNM | Trichloronitromethane | (µg/l) |
| THM | Trihalomethane | (µg/l) |
| $THM_4$ | Sum of four THMs (TCM, BDCM, DBCM and TBM) | |
| THM-FP | Trihalomethane Formation Potential | |
| TIM | Triiodomethane | (µg/l) |
| TOBr | Total Organic Bromine | (µg/l) |
| TOC | Total Organic Carbon | (mg/L) |
| TOCl | Total Organic Chlorine | (µg/l) |
| TOI | Total Organic Iodine | (µg/l) |
| TOX | Total Organic Halogen | (µg/l) |
| TPI | Transphilic | |
| TXAA | Trihalogenated Acetic Acid | (µg/l) |
| UK | United Kingdom | |
| UNC | University of North Carolina | |
| US | United States | |
| US EPA | United States Environmental Protection Agency | |

| | | |
|---|---|---|
| UV | Ultraviolet | (1/m) |
| $UV_{254}$ | Ultraviolet absorbance at 254 nm | (1/m) |
| WHO | World Health Organisation | |
| WTW | Water Treatment Works | |

**Notation**

| | | |
|---|---|---|
| A | Reactant for kinetic reaction | |
| α | THM yield coefficient | (µg THM/mg $Cl_2$) |
| $A_{DBP}$ | Peak area of DBP | |
| $A_{HAA}$ | Peak area of HAA | |
| $A_{IS}$ | Peak area of internal standard | |
| At | Millilitre standard acid titrant | |
| B | Reactant for kinetic reaction | |
| β | HAA yield coefficient | (µg HAA/mg $Cl_2$) |
| $C_0$ | Initial chlorine concentration | (mg/L) |
| C(t) | Chlorine concentration at any time | (mg/L) |
| $C_{DBP}$ | Concentration of DBP | (µg/l) |
| $C_{HAA}$ | Concentration of HAA | (µg/l) |
| D | Concentration fortified sample | (µg/l) |
| E | Concentration unfortified sample | (µg/l) |
| F | Fortified concentration | (µg/l) |
| f | Fraction of chlorine demand attributed to rapid reactions | |
| $k_1$ | Constant of $1^{st}$ order kinetic reaction | |
| $k_2$ | Constant of $2^{nd}$ order kinetic reaction | |
| k’ | Column capacity factor | |
| $k_R$ | $1^{st}$ order rate constant for rapid reactions | ($h^{-1}$) |
| $k_S$ | $1^{st}$ order rate constant for slow reactions | ($h^{-1}$) |
| N | Normality | |
| n | Number of replicates | |
| $R^2$ | Coefficient of correlation | |

| | | |
|---|---|---|
| S | Standard deviation of replicate analysis | |
| T | Temperature | (ºC) |
| t | Time | (hours) |
| $t_{(n-1,1-\alpha=0.99)}$ | Student t value for the 99% interval confidence level with n-1 degrees of freedom | |

# Chapter 1

# INTRODUCTION

## 1.1 PROJECT BACKGROUND

Disinfection by-products (DBPs) were first discovered in the 1970s in chlorinated drinking water (Bellar et al., 1974; Rook, 1974) and consequently, the use of chlorine as a disinfectant has come under investigation. Chlorine reacts with the natural organic matter (NOM) ubiquitous in water to form DBPs, which can take the form of trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloacetaldehydes (HAs), halonitromethanes (HNMs) and a host of other halogenated DBPs (Richardson et al., 2007). Many of these DBPs have been shown to be cytotoxic, genetoxic or to cause cancer in laboratory animals, and are as such a public health concern (Bull et al., 1990; Plewa et al., 2002).

Richardson (1998) reported approximately 500 DBPs in drinking water of which the most prevalent groups are the THMs and the HAAs (Singer, 2002). In the United Kingdom (UK), THMs are the only regulated DBPs and it is required by law that the sum of four THMs (trichloromethane – TCM, bromodichloromethane – BDCM, dibromochloromethane – DBCM and tribromomethane – TBM) does not exceed 100 µg/L with a frequency of sampling dependent on the population size (DWI, 2005). In the United States (US), the US Environmental Protection Agency (US EPA) has established maximum contaminant levels (MCLs) of 80 µg/L for four THMs and 60 µg/L for five HAAs (monochloro-, monobromo-, dichloro-, trichloro- and dibromoacetic acid (MCAA, MBAA, DCAA, TCAA and DBAA)) (US EPA, 1998). HAAs are currently not regulated in the UK, however, the European Union is considering regulating the nine HAAs at 80 µg/L (Cortvriend, 2008) and as such there is growing interest in the levels of these compounds found in UK drinking waters and how best to control them.

One option which would help the water utilities to comply with these proposed regulations, would be to use monochloramine as a secondary disinfectant, as it

has been shown to reduce DBP formation and also, like chlorine provides a residual in water distribution systems. However, the use of monochloramine may also lead to an increase in other DBPs such as HANs and i-THMs (Krasner et al., 1989; Bichsel and Von Gunten, 2000). HANs and i-THMs are two unregulated classes of semi-volatile DBPs also present in disinfected waters alongside other unregulated DBPs including HNMs, HAs and HKs (Krasner et al., 2006). Many of these DBPs have been reported to be more cytotoxic and genetoxic than some of the regulated DBPs, and the brominated DBPs are in general more genetoxic and carcinogenic than are the chlorinated compounds, and the iodinated DBPs are the most genotoxic (Richardson et al., 2007; Plewa et al., 2008). Little is known about the formation of semi-volatile DBPs in UK waters.

## 1.2 MOTIVATION FOR WORK

The work presented in this thesis brought together five UK water companies, concerned by emerging DBPs: Anglian Water, Northumbrian Water Limited, Severn Trent Water, United Utilities and Yorkshire Water.

In 2005, a study on HAAs and THMs has been commissioned by the five water companies cited above plus Thames Water, with objective to determine the relative distribution and speciation of THMs and HAAs in a variety of UK water treatment works (WTWs) (confidential, not published). Sampling was undertaken seasonally, and both groups of species were measured in WTW final treated water and distribution samples. In addition, THM and HAA formation potential (FP) was determined under controlled uniform conditions. Initial results showed that some final waters had concentrations of HAAs between 180 and 265 µg/L (Figure 1.1), well above the regulations promulgated in the US, and as such identified a need for a more detailed investigation.

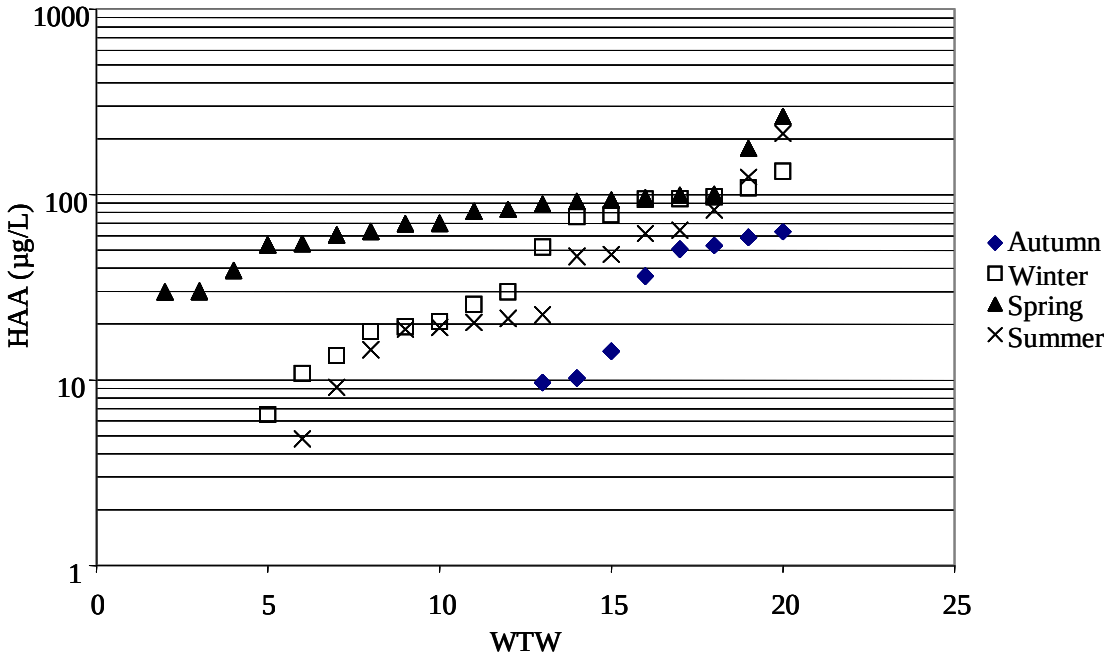



Figure 1.1 Seasonal variations in HAA formation

The main conclusion from this work was that many water quality and treatment factors influence the distribution of THMs and HAAs in drinking water. Nevertheless, it was difficult to determine any strong relationship between any water parameters and HAA and THM formation. Another UK study on HAAs and THMs, undertaken by Malliarou et al. (2005), reported HAAs with mean levels in the UK ranging from 35 to 95 µg/L and a maximum concentration of 244 µg/L.

To investigate further the formation and occurrence of DBPs, it was deemed necessary to set up convenient and sensitive methods for the determination of DBPs in UK drinking water. Clearly, effective monitoring of DBPs should enable a better understanding of DBPs and hence, lead to an optimisation of water treatments and better control of these DBPs.

## 1.3 PROJECT AIMS AND OBJECTIVES

The purpose of this thesis was to broaden the understanding of DBP-FP of UK treated waters with reliable and reproducible methods in order to optimise their control in WTWs and therefore, to meet THM regulations and to anticipate the HAA ones.

Consequently, a series of objectives were identified:

- To determine the best analytical method for the measurement of HAAs in UK treated waters.
- To broaden the number of DBPs analysed and therefore, set up reliable and reproducible method for their determination.
- To compare the impact of the choice of disinfectant on the level of DBP formed.
- To assess the important parameters affecting the formation of THMs and HAAs.
- To determine if correlations exist between water characteristics and DBP-FP.
- To determine precursors for HAAs and possible common precursors between waters.

## 1.4 THESIS PLAN AND PUBLICATIONS

Initially, a literature review was carried out (Chapter 2) to determine methods of analysis to determine HAAs and other DBPs in treated and drinking waters. This literature review also emphasises the formation, occurrence and precursors of DBPs in the US waters, but shows a lack of data for the UK waters, where water treatments are not necessarily similar to those applied in US WTWs.

Chapter 3 to Chapter 6 cover the technical content of this thesis and the link between the chapters are presented in a flow chart (Figure 1.2). Chapter 3 assess the different analytical methods available for the measurement of HAAs. Four methods have been investigated, from which the most reliable and reproducible has been chosen and validated for quantification of HAAs in UK treated waters. The first part of this chapter describing the method comparison has been presented as a paper at an international conference (Bougeard, C. M. M., Janmohamed, I. H. S., Goslan, E. H., Jefferson, B., Watson, J. S., Morgan, G. H. and Parsons, S. A. (2007). Occurrence of Trihalomethanes (THMs) and Haloacetic Acids (HAAs) in UK waters. In: 233rd National Meeting of American Chemical Society Division of Environmental Chemistry, 27-29 March, Chicago, IL, US.) and later published: Bougeard, C. M. M., Janmohamed, I. H. S., Goslan, E. H., Jefferson, B., Watson, J. S., Morgan, G. H. and Parsons, S. A. (2008). In*:*

*Disinfection By-Products in drinking Water: Occurrence, Formation, Health Effects, and Control*. American Chemical Society Symposium Series 995, edited by Karanfil, T., Krasner, S. W., Westerhoff, P. and Xie, Y. Washington, DC, US, p. 95-108. The first part of the book chapter highlighted which methods fitted the best to the quantification of HAAs in treated waters.

Chapter 4 shows the interest of the author in DBPs other than HAAs, and demonstrates that i-THMs, HANs, HAs, HKs and HNMs could also be found in UK treated waters. Therefore, in this chapter, it is shown the qualitative identification of these compounds and the development of an analytical method for their quantification. This work was presented at an international conference as a paper (Bougeard, C. M. M., Goslan, E. H., Jefferson, B., Parsons, S. A. (2008). Disinfection by-products (DBPs) in UK drinking water. In: International Conference on Emerging Issues in Disinfection By-Products, 3rd April, Cranfield, UK). The method developed here was also published jointly with Chapter 5.

Chapter 5 reports an investigation of 11 WTWs across England and Wales for their potential to form HAAs, THMs and other halogenated DBPs using chlorine and preformed monochloramine. To allow this work, methods developed and set up in Chapter 3 and Chapter 4 were used. This chapter has been submitted as paper format, jointly with the method description of Chapter 4: Bougeard, C. M. M, Goslan, E. H., Jefferson, B., Parsons, S.A. Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water Research.*

Chapter 6 is a more detailed study on the formation of HAAs and THMs. Because THMs are regulated and HAAs are under consideration for regulation, it was important to determine the parameters that affect the most their formation. This work was presented alongside the results from Chapter 3 at the 233rd National Meeting of American Chemical Society Division of Environmental Chemistry, and later published in the same book chapter cited above. An investigation of the precursor reactivity towards the formation of HAAs is also investigated in this chapter. Finally, a mathematical approach is presented to study the kinetics of chlorine decay and a model was adapted to UK treated waters for the prediction of THMs and HAAs. The work related to the chlorine decay was part of a poster presentation at an international

conference (Bougeard, C. M. M, Goslan, E. H., Jefferson, B., Parsons, S.A. (2006). In: Gordon Conference in Drinking Water Disinfection By-Products, 13-18 August, South Hadley, MA, US).

The overall implications of this research are pulled together in Chapter 7 "Recommendations for water utilities" and key conclusions from this thesis are made (Chapter 8).

Suggestions for further work are reported in Chapter 9.

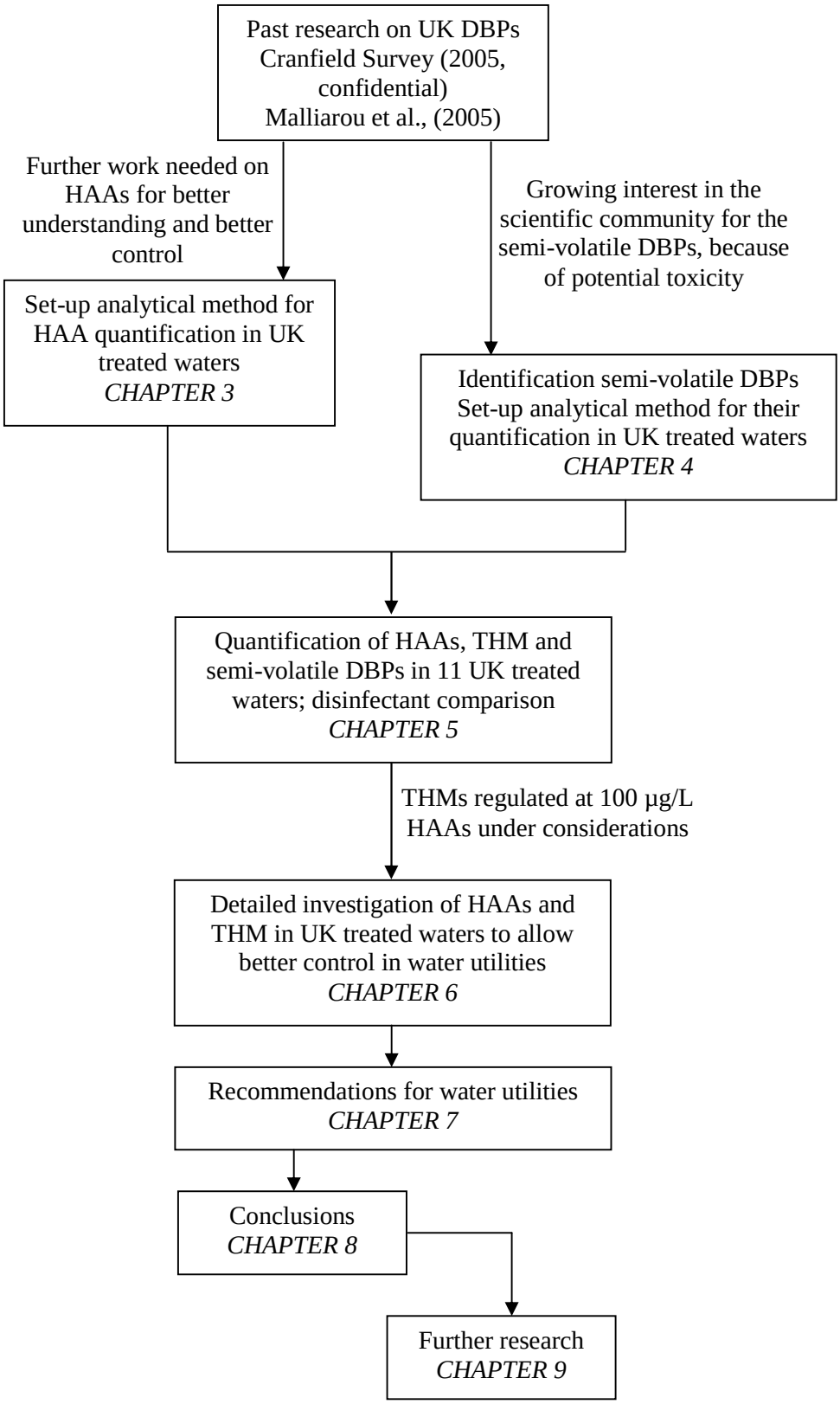



Figure 1.2 Flow chart of the Phd

# Chapter 2

# LITERATURE REVIEW

## 2.1 INTRODUCTION

DBPs in drinking water were first discovered in the 1970s and the first public health concern was raised with the identification of TCM and other THMs in chlorinated water (Bellar et al., 1974; Rook, 1974). Since that, more than hundreds of DBPs have been found in drinking water (Richardson et al., 1998). The most prevalent chlorinated DBPs are the THMs and the HAAs, comprising more than 50% on a weight basis, followed by trichloroacetaldehyde (TCA - HAs), HANs, HKs and HNMs (Singer et al., 2002). All these chemicals, plus the iodinated counterparts of THMs (i-THMs), have been detected in drinking water that has been treated using the most common disinfectants (chlorine, chloramines, ozone and chlorine dioxide) (Krasner et al., 2006).

Because of their potential health concern, HAAs and THMs are regulated in the US at 60 µg/L and 80 µg/L respectively (US EPA, 1998). In the UK, only THMs are regulated at a concentration of 100 µg/L (DWI, 2005). To date, no regulations have been promulgated for HAs, HANs, HKs, HNMs and i-THMs, despite their toxicity (Plewa et al., 2004; Plewa et al., 2008), but the World Health Organisation (WHO) has suggested guideline values of 20 µg/L for dichloroacetonitrile (DCAN), 70 µg/L for dibromoacetonitrile (DBAN) and 10 µg/L for TCA (WHO, 2006).

DBPs are formed when NOM that remains after treatment processes reacts with the disinfectants. Therefore, to have a better understanding of DBP formation and occurrence, a significant amount of research has been conducted with the aim to identify the DBP levels and their precursors, the reaction pathways and the physical parameters that lead to DBP formation. DBP precursors can be organic, such as the nature and concentration of NOM, or inorganic, such as bromide and/or iodide present in the natural water source (Cowman and Singer, 1996; Bichsel and Von Gunten, 2000; Hwang et al., 2001; Goslan et al., 2002). Physical parameters, such as the pH, the type of disinfectants, the contact time, the temperature and the disinfectant dose have also

been extensively studied and are well known to alter the formation of HAAs and THMs (Carlson and Hardy, 1998; Singer, 1999; Diehl et al., 2000; Malliarou et al., 2005).

The aim of this review is to give insight into the occurrence and the formation of HAAs, THMs and other DBPs, present in drinking and/or treated water, with a particular emphasis on the precursors and the factors involved in the formation of HAAs and THMs. Analytical methods for the determination of DBPs in drinking and/or treated water are also assessed. Hence, by determining suitable analytical methods and the parameters that affect the most the DBP formation in drinking and/or treated water, it is hope to aid the water companies to adapt their treatments to minimise or to better control the DBP formation.

## 2.2 BACKGROUND

### 2.2.1 Aqueous chlorine chemistry

Chlorine (from the Greek word "χλωρός" (*khlôros)*, meaning pale green), under standard pressure and temperature, is a pale green gas ($Cl_2$ or dichlorine), characterised by a disagreeable suffocating odor that is poisonous (WHO, 1998). Chlorine exists also predominantly in nature as chloride ion ($Cl^-$), a trace component of all the earth's geological compartment other than the oceans, its primary sink (Winterton, 2000).

Chlorine, in the form of gaseous chlorine ($Cl_2$) or sodium hypochlorite (NaOCl), is a powerful oxidant and is used as water purification, despite the formation of potentially harmful DBPs associated with its use (Deborde and Von Gunten, 2008).When chlorine gas is dissolved in water, it hydrolyses rapidly to yield hypochlorous acid (HOCl) as:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- . \qquad \text{Equation 2.1}$$

Hypochlorous acid is also formed when sodium hypochlorite (NaOCl) is used as the source of chlorine:

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^- . \qquad \text{Equation 2.2}$$

Hypochlorous acid is a weak acid (pKa = 7.6) and dissociates partially into hydrogen ion ($H^+$) and hypochlorite ion ($OCl^-$) in the reversible reaction:

$$HOCl \Leftrightarrow H^+ + OCl^- . \qquad \text{Equation 2.3}$$

Under typical water treatment conditions in the pH range 6 to 9, hypochlorous acid and hypochlorite ion, both will be present in the water in a proportion dependent of the temperature (Deborde and Von Gunten, 2008). Hypochlorous acid is a more effective disinfectant than hypochlorite ion. Another reaction that occurs in waters containing bromide ion ($Br^-$) and hypochlorous acid is the formation of hypobromous acid (HOBr) (Von Gunten and Oliveras, 1998):

$$HOCl + Br^- \rightarrow HBrO + Cl^- . \qquad \text{Equation 2.4}$$

Hypobromous acid and hypobromite ion ($OBr^-$) have a pKa of 8.7.

In any case, chlorine or bromine substitution can lead to the formation of DBPs when NOM is present in the water.

### 2.2.2 Chloramine chemistry

Chloramine chemistry can be summarised by three reversible reactions involving ammonia ($NH_3$), hypochlorous acid, monochloramine ($NH_2Cl$), dichloramine ($NHCl_2$), and trichloramine ($NCl_3$) (Diehl et al., 2000):

$$NH_3 + HOCl \Leftrightarrow NH_2Cl + H_2O , \qquad \text{Equation 2.5}$$

$$NH_2Cl + HOCl \Leftrightarrow NHCl_2 + H_2O , \qquad \text{Equation 2.6}$$

$$NHCl_2 + HOCl \Leftrightarrow NCl_3 + H_2O . \qquad \text{Equation 2.7}$$

The competing reactions are highly dependent upon pH, the ratio of chlorine to ammonia-nitrogen (or chlorine to nitrogen ratio expressed as $Cl_2$:N), and to a lesser degree, temperature and contact time. A typical distribution of chloramine species as a function of pH is shown (Figure 2.1). Experimental conditions were 2.5 mg/L of chlorine in contact with 0.5 mg/L of ammonia (5:1 $Cl_2$:N weight ratio) for two hours (Kirmeyer et al., 2004). The authors observed that, for the pH range normally encountered in drinking water treatment (optimum pH condition 6.5 – 9), almost all of the chloramine species consist of monochloramine, while at pH less than 6, dichloramine generally accounts for 20 percents or more of the chloramines formed. The maximum synthesis of dichloramine occurs at a pH range of 4 to 6 and $Cl_2$:N weight ratio of 5:1 to 7.6:1.

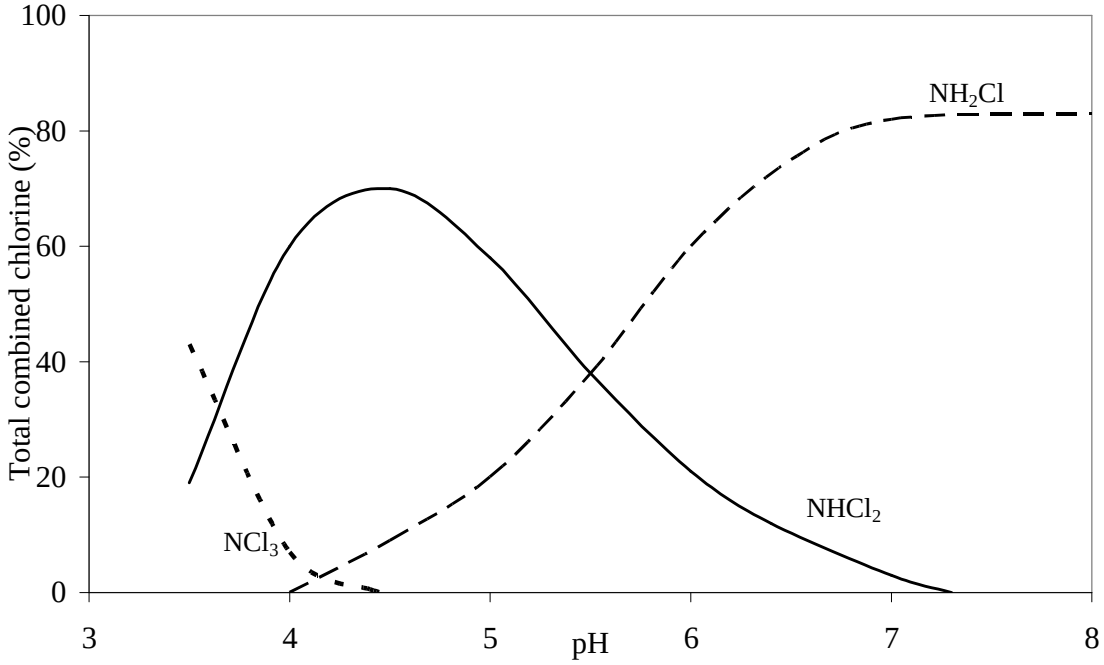



Figure 2.1 Distribution of chloramine species as a function of pH (Kirmeyer et al., 2004)

The formation of trichloramine (Equation 2.7) occurs predominantly at pH values less than 4.4 (Figure 2.1) or at $Cl_2$:N weight ratio greater than 7.6:1 (Kirmeyer et al., 2004). Trichloramine in drinking water systems may be formed at trace levels following the breakpoint chlorination (White, 1999).

*Breakpoint chlorination*

The breakpoint chlorination occurs when enough chlorine has been added to meet the chlorine demand of the water and oxidises all the ammonia. Therefore, chlorine that is added beyond that point (theoretically a weight ratio of 7.6:1 $Cl_2$:N) remains present in the water as free chlorine residual and mono-, di- and trichloramine may be only present as trace levels (Wolfe et al., 1984). Summary of the residual species present in water as a function of $Cl_2$:N ratio is presented below (Figure 2.2).

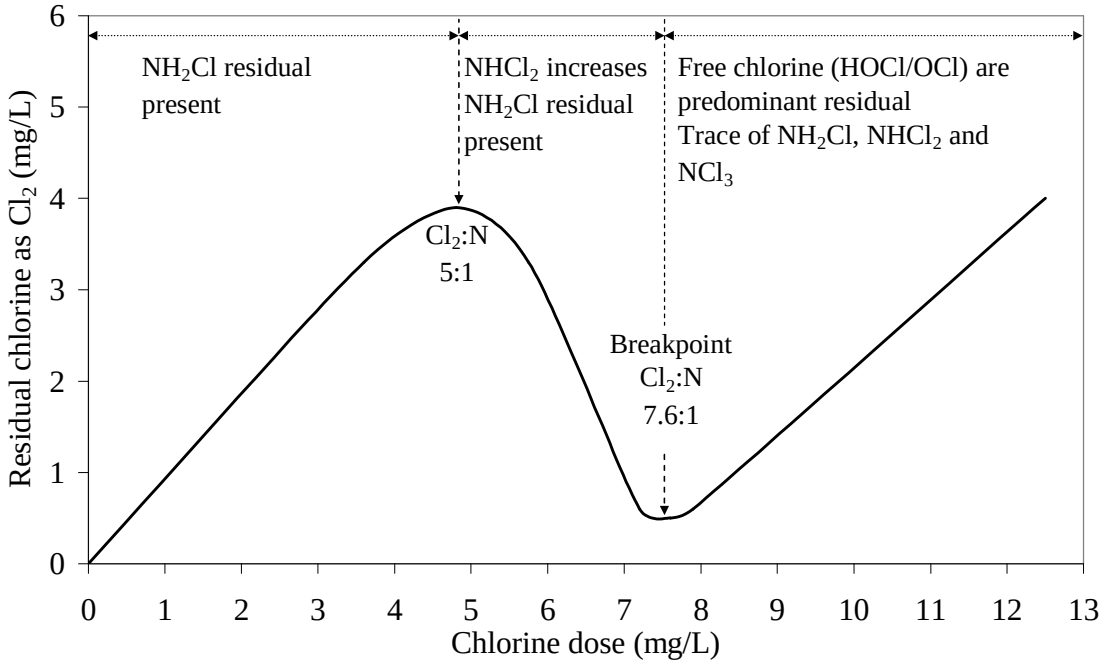



Figure 2.2 Breakpoint chlorination scheme (1.0 mg/L nitrogen, temperature 25°C, contact time 2 hours) (Wolfe et al., 1984)

Monochloramine, the only used disinfectant amongst chloramine species, has a much higher CT value[1] than free chlorine and is therefore a poor primary disinfectant (WHO, 2000). However, because of its persistence, it is an attractive secondary disinfectant for the maintenance of a stable distribution system residual. Di- and trichloramine are too unstable and highly malodorous to be used as disinfectants.

### 2.2.3 NOM

NOM, ubiquitous in drinking water, is of concern because it serves as precursor to the formation of DBPs. It has been extensively studied, but still remains a complex and heterogeneous mixture of specific but mostly hard-to-identify compounds and varies significantly from one source to another (Hwang et al., 2001). The same author defined NOM as a mixture of two separate fractions: the hydrophobic (non-polar) substances, generally of terrestrial origin and the hydrophilic (polar) substances, typically of

[1] The CT value is the product of the disinfectant concentration C in mg/L and the contact time T in minute required to inactivate a specified percentage of microorganisms (WHO, 2000).

biological origin. To better understand the reactivity of NOM towards the formation of DBPs, NOM is generally characterised by measuring its total organic carbon (TOC) or dissolved organic carbon (DOC) concentration, its ultraviolet (UV) absorbance, generally at 254 nm to exhibit the amount of aromatic material, and its potential to form DBPs (see Section 2.3.4.1). The fractionation and isolation of DBP NOM precursor with XAD 8 / 4 resins have also been used to determine which fractions of NOM contribute the most to the DBP formation (Oliver and Thurman, 1983; Reckhow and Singer, 1990; Croué et al., 1993). However, most of these works focused on NOM from untreated water and therefore, a lack of results remains on NOM fractions that remain after treatment in drinking water and their reactivity towards DBPs. An overview on drinking water NOM fractions and their impact on DBPs are given in Section 2.3.4.2.

## 2.3 HAA AND THM OCCURRENCE AND FORMATION FROM DRINKING WATER

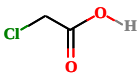
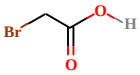
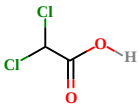
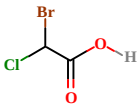
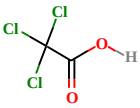
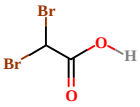
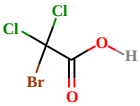
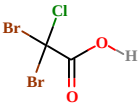
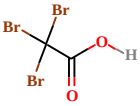
The first DBPs to be identified and regulated in drinking water were the THMs (Symons, 1999). These are trichloromethane (TCM or chloroform), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM or bromoform). Their molecular formula, their molecular weight, their structure, their boiling point and their CAS number are given (Table 2.1). These four THMs are often referred as $THM_4$.

Table 2.1 Chemical and physical properties of THMs

| THM | Molecular formula | Molecular weight (g/mol) | Structure | Boiling point (°C) | CAS number |
|---|---|---|---|---|---|
| TCM | $CHCl_3$ | 119.38 |  | 61-62 | 67-66-3 |
| BDCM | $CHBrCl_2$ | 163.83 |  | 87 | 75-27-4 |
| DBCM | $CHBr_2Cl$ | 208.28 |  | 119-120 | 124-48-1 |
| TBM | $CHBr_3$ | 252.73 |  | 146-150 | 75-25-2 |

The second most abundant DBPs found in drinking water are the HAAs and there are nine chloro- and bromo-HAAs in total (Singer, 2002). They are classified as monohalogenated acetic acid (MXAA or XHAA) (monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA)), dihalogenated acetic acid (DXAA or $X_2AA$) (dichloroacetic acid (DCAA), dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA)) and trihalogenated acetic acid (TXAA or $X_3AA$) (trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA) and tribromoacetic acid (TBAA)). US regulation is currently in place for five of the HAAs. These are MCAA, MBAA, DCAA, TCAA and DBAA and are often referred as $HAA_5$. All nine HAAs are referred as $HAA_9$ for measurement purpose; nevertheless, six HAAs are often determined ($HAA_5$ + BCAA) and are called $HAA_6$. Their molecular formula, their molecular weight, their structure, their boiling point, their respective methyl ester boiling point and their CAS number are given (Table 2.2). The boiling point of methyl esters is shown as the HAAs are converted to their methyl ester form before gas chromatography (GC) analysis (Chapter 3).

Table 2.2 Chemical and physical properties of HAAs

| HAA | Molecular formula | Molecular weight (g/mol) | Structure | Boiling point (°C) | Boiling point of ester (°C) | CAS number |
|---|---|---|---|---|---|---|
| MCAA | $C_2H_3ClO_2$ | 94.45 |  | 189 | 130 | 79-11-8 |
| MBAA | $C_2H_3BrO_2$ | 138.95 |  | 206-208 | 132 | 79-08-3 |
| DCAA | $C_2H_2Cl_2O_2$ | 128.94 |  | 194 | 143 | 79-43-6 |
| BCAA | $C_2H_2BrClO_2$ | 173.39 |  | 215 | 174 | 5589-96-8 |
| TCAA | $C_2HCl_3O_2$ | 163.39 |  | 196 | 168 | 76-03-9 |
| DBAA | $C_2H_2Br_2O_2$ | 217.84 |  | 128-130 | NR[a] | 631-64-1 |
| BDCAA | $C_2HBrCl_2O_2$ | 207.84 |  | NR[a] | NR[a] | 71133-14-7 |
| DBCAA | $C_2HBr_2ClO_2$ | 252.29 |  | NR[a] | NR[a] | 5278-95-5 |
| TBAA | $C_2HBr_3O_2$ | 296.74 |  | 245 | 225 | 75-96-7 |

[a] Not reported.

### 2.3.1 Toxicity and regulations

DBPs were first discovered in drinking water in 1974 (Bellar et al., 1974; Rook, 1974) in the form of THMs. As a response, toxicological evaluations have been undertaken and first concern for public health arised. Indeed, in 1976, a National Cancer Institute (NCI) study was released in which TCM (chloroform) was classified as a suspected human carcinogen. Following this finding, studies on rats and mice linked THMs to cancers of the colon and the kidneys and HAAs to liver tumours (Dunnick, 1985; Bull et al., 1990; Boorman et al., 1999). Kargalioglu et al. (2002) also reported MCAA, DCAA, TCAA, BCAA, DBAA and TBAA to be cytotoxic (toxic to cells) and

mutagenic (modify the genetic material) in *Salmonella typhimurium*. There is a general opinion that the brominated HAAs are more cytotoxic and genetoxic (cause damage to deoxyribonucleic acid – DNA) than their chlorinated analogues while working with Chinese hamster ovary (CHO) cells (Plewa et al., 2002).

The risk of human cancer from DBPs, especially cancers of the colon, the rectum and the bladder have been documented by several epidemiological studies (King and Marret, 1996; Doyle et al., 1997; Koivusalo et al., 1997; Cantor et al., 1998; Hidelsheim et al., 1998). There are ongoing concerns that the types of cancer observed in animal studies for the DBPs that have been tested do not correlate with the types observed in human epidemiological studies (bladder, colon cancer) (Richardson, 1998). Nevertheless, several epidemiological studies have reported DBPs to be potentially harmful to foetuses, such as THMs being linked to the frequency of stillbirths or having a strong association to spontaneous abortions (Waller et al., 1998; King et al., 2000; Bove et al., 2002).

To respond to these toxicological and epidemiological studies, the US EPA was actively prompted to publish regulation and started in 1979 by setting a MCL for THMs as annual average of 100 µg/L. In 1998, the US EPA strengthened existing rules with its Stage 1 Disinfectants and Disinfection Byproducts, reducing the MCL for the four THMs ($THM_4$: TCM, BDCM, DBCM and TBM) to 80 µg/L and including contaminant level for the sum of the five HAAs ($HAA_5$: MCAA, MBAA, DCAA, DBAA and TCAA) at 60 µg/L. Despite all these efforts, these regulations are believed to not be strong enough and one study of Singer (2006) entitled “Regulation of Only Five Haloacetic Acids is Neither Sound Science Nor Good Policy” expressed the confusion of regulating only five HAAs and illustrated situations where overall HAA concentration and HAA exposure have been under-estimated and have led to confusion and incorrect interpretation of data. UK regulations have focused so far on THMs and state a maximum level of 100 µg/L with a frequency of sampling dependant of the population size (DWI, 2005). In regards to the HAA, the European Union is considering regulating the nine HAAs at 80 µg/L (Cortvriend, 2008).

### 2.3.2 Analytical measurement

*HAAs*

HAAs are a group of anions that can be found at levels significantly above the US EPA regulatory limits and therefore to monitor their level in drinking water, several analytical methods have been developed:

- Gas chromatography – electron capture detector (GC/ECD),
- Gas chromatography – mass spectrometry (GC/MS),
- Ion chromatography (IC),
- Capillary electrophoresis (CE) and capillary zone electrophoresis (CZE),
- High performance liquid chromatography (HPLC) and
- Electrospray ionization – mass spectrometry (ESI/MS).

Examples of published limits of detection (LOD) from each method have been collated (Table 2.3). Their sample preparation and the number of HAA detected have also been reported.

The GC/ECD method is the most widely applied and to date the US EPA has set four approved methods: the US EPA Method 552.1 (1992), the US EPA Method 552.2 (1995), the US EPA Method 552.3 (2003) and the Standard Method 6251 (APHA, 1998). In these methods, HAAs are extracted from water samples using either methyl tert-butyl ether (MtBE) or anion exchange resins, and then converted to their methyl esters using acidic methanol or diazomethane. The GC/ECD US EPA methods are typically reliable and accurate with detection limits for the nine HAAs in the low µg/L range, but on the other hand, they involve labour intensive extraction procedures and the use of toxic derivatisation reagents.

William et al. (1997), Scott et al. (2000) and Xie (2001) determined the HAA concentrations by GC/MS. This method also requires the conversion of HAAs to their methyl ester forms. The advantages of the method are (1) the fewer interfering peaks than with GC/ECD, (2) clean baselines and (3) the use of short run time without compromising the analytical results (Xie, 2001). On the other hand, the method shows a low sensitivity for brominated species (Xie, 2001).

Liu and Mou (2003) were the first to report the IC method, which is a short method due to the limited sample preparation. The nine HAAs can be detected but the sensitivity of the method remains poorer than that of the GC/ECD ones.

Other methods reported for the quantification of HAAs in drinking water include CE or CZE, HPLC and ESI/MS (Skelly, 1982; Nair et al., 1994; Vichot and Furton, 1994; Xie and Romano, 1997; Carrero and Rusling, 1999; Urbansky, 2000; Xie et al., 2000; Kim et al., 2001). CE, CZE and HPLC are short methods (less than 10 minutes to separate $HAA_9$), but they allow detection only in the mg/L range or in medium µg/L range. On the other hand, ESI/MS is a very sensitive and selective method that achieves detection limits of ≤ 70 ng/L. However, the cost of the instrumentation contributes to its lack of availability in research laboratories.

*Concluding comments*

HAA levels expected to be in the mg/L range, such as in biodegradation work, will be easily analysed with HPLC or IC (Hozalski et al., 2001; McRae et al., 2004). However, the concentration of HAAs in drinking and/or treated water is expected to be in the low µg/L range (trace levels) and hence, the use of GC/ECD or GC/MS is more suitable than IC, CE or HPLC.

Table 2.3 Analytical method, description, and limit of detection

| Measuring device | Sample Preparation | Instrumental analysis time | Limit of detection (µg/L) (recovery, when applicable, %) | HAA detected | Reference |
|---|---|---|---|---|---|
| GC/ECD | *Extensive preparation* Derivatisation (extraction + methylation) US EPA method protocols | > 55 min | 0.820 – 0.066 (84.7 – 107) | $HAA_9$ | US EPA method 552.2 (1995) - US |
| | | | 0.012 – 0.170 (97.8 - 108) | $HAA_9$ | US EPA method 552.3 (2003) - US |
| | | | 0.4 – 1.3 | $HAA_6$ (BDCAA instead of MCAA) | Malliarou et al. (2005) – UK |
| | | | 0.6 – 1.3 | $HAA_6$ | Rodriguez et al. (2004) – Canada |
| | | | 0.066 – 0.820 | MBAA, DCAA, TCAA, DBAA, TBAA | Marhaba and Van (2000) – US |
| | | | NR[a] (52 – 105) | $HAA_9$ | Pourmoghaddas et al. (1993) – US |
| GC/MS | *Extensive preparation* Derivatisation (extraction + methylation) | < 55 min | 0.07 – 0.83 (73 – 165) | $HAA_9$ | Xie (2000) – US |
| | US EPA method protocols + Method from Scott and Alaee (1998) | | 0.001 – 0.050 | MCAA, MBAA, DCAA, DBAA | Scott et al. (2000) – Canada |
| IC | *Minimal preparation* Cartridges to remove chlorine and silver | < 40 min | 0.37 – 31.6 (96.6 – 99.1) | $HAA_9$ | Liu and Mou (2003) – China |
| CE | *Moderate preparation* Filatration through a 0.45 µm pore size filter capsule | < 10 min | 683 – 1507 | $HAA_9$ | Hozalkski et al. (2001) – US |
| | | | 140 – 1062 | MCAA, MBAA, TCAA | McRae et al. (2004) – US |

| Measuring device | Sample Preparation | Instrumental analysis time | Limit of detection (µg/L) (recovery, where applicable, %) | HAA detected | Reference |
|---|---|---|---|---|---|
| HPLC | *Moderate preparation* Skelly's procedure (1982) | < 10 min | 30 – 40 | DCAA, DBAA, TCAA, TBAA | Heller-Grossman et al. (1993) – Israel |
| HPLC/EC | *Moderate preparation* Direct evaporation and solid phase extraction (SPE) | < 30 min | 120 – 10000 | $HAA_6$ (TBAA instead of DBAA) | Carrero and Rusling (1999) – US |
| ESI/MS | *Extensive preparation* Extraction as for GC/ECD | < 10 min | ≤ 70 ng/L | NR[a] | Urbansky (2000) – US |

[a] Not reported.

*THMs*

THMs are volatile and they can be "stripped" from the water into GC gas phase. In the US there are three approved methods for THM analysis (US EPA, 1995a, 1995b, 1995c). Both US EPA 502.2 (1995b) and 524.2 (1995c) are purge and trap (P&T) GC methods. US EPA method 551.1 (1995a) uses liquid-liquid extraction (LLE) before analysis by GC/ECD. There are also three Standards Methods for the analysis of THMs (6232B, 6232C and 6232D) (APHA, 1998), which are similar to the US EPA ones but they are not listed as approved methods (Xie, 2003).

### 2.3.3 Typical levels in drinking water

HAAs and THMs are by far the most abundant DBPs in drinking water and HAAs can be found equal to, or greater than the concentration of THMs (Singer, 2002). The range of HAA and THM worldwide concentrations reported in drinking water have been summarised (Table 2.4).

HAAs and THMs have been extensively studied in the US, where several national occurrence studies have been undertaken (Krasner et al., 1989; McGuire et al., 2002; Weinberg et al., 2002; Krasner et al., 2006). For example, Krasner et al. (1989), in their survey encompassing 35 water treatment utilities, found median total THM concentration ranged from 30 to 44 µg/L, with TCM, BDCM, DBCM and TBM from 9.6-15, 4.1-10, 2.6-4.5 and 0.33-0.88 µg/L respectively and median total $HAA_5$ concentration ranged from 13 to 21 µg/L, with MCAA, MBAA, DCAA, TCAA and DBAA from <1-1.2, <0.5, 5.0-7.3, 4.0-6.0 and 0.9-1.5 µg/L respectively. Recently another survey by Krasner et al. (2006) reported median average $HAA_9$ concentration, in 12 differently treated drinking waters, to be 34 µg/L and 31 µg/L for median average THM concentration from the same utilities.

In the UK, one study reported levels of HAAs and THMs on a regional basis, with HAA means ranging from 35 to 95 µg/L per region (Table 2.4) (Malliarou et al., 2005).

In most of the surveys cited (Table 2.4), DCAA, TCAA and TCM are the most important species, with DCAA and TCAA similar to the concentrations of TCM. Furthermore, HAA and THM concentrations have been shown to be affected by

seasonal variation with the highest concentrations found in summer (Krasner et al., 1989; Singer et al., 1995; Williams et al., 1997; Dojlido et al., 1999).

Table 2.4 Reported levels of HAAs and THMs in drinking and/or treated water

| Reference | Location | Water source | HAA | | $THM_4$ |
|---|---|---|---|---|---|
| | | | HAA measured | Range (µg/L) | Range (µg/L) |
| Malliarou et al. (2005) | UK | Drinking water | $HAA_9$ | NR[a]-244 | NR-76 |
| Nissinen et al. (2002) | Finland | Drinking water | $HAA_6$ | 6.00-261 | 1.00-103 |
| Peters et al. (1991) | Netherlands | Drinking water | $HAA_9$ | 0.00-14.7 | NR[a] |
| Cancho et al. (1999) | Spain | Drinking water | $HAA_9$ | 11.0-32.0 | 58.0-91.0 |
| Dojlido et al. (1999) | Poland | After chlorination | $HAA_6$ | 10.0-120 | 2.00-110 |
| Williams et al. (1997) | Canada | Drinking water | MCAA<br>MBAA<br>DCAA<br>TCAA<br>DBAA | 0.30-10.0<br>0.01-9.00<br>0.20-163<br>0.04-473<br>0.01-2.00 | 0.30-342 |
| Krasner et al. (1989) | US | Drinking water | $HAA_5$ | 13.0-21.0 | 30.0-44.0 |
| Krasner et al. (2006) | US | Drinking water | $HAA_9$ | 5.00-130 | 4.00-164 |
| Ates et al. (2007) | Turkey | Filtered surface water | $HAA_9$ | 6.00-177 | 13.0-191 |
| Wang et al. (2007) | China | Drinking water | $HAA_6$ | 0.40-14.0 | 3.00-16.0 |

[a] Not reported.

Several studies looked at the correlation between HAAs and THMs (Nissinen et al. 2002; Liang and Singer, 2003; Malliarou et al., 2005; Ates et al., 2007). For example Ates et al. (2007) found a strong correlation between HAAs and THMs with a coefficient of correlation ($R^2$) of 0.87, whereas Nissinen et al. (2002) found an $R^2$ of 0.35 (Figure 2.3). In their study, Malliarou et al. (2005) found an $R^2$ of 0.56 for one of the regions they investigated. However, they also reported that in another region, no correlation could be found between HAAs and THMs. A good correlation between THMs and HAAs can be useful for quality control and monitoring in water utilities because, in general, laboratory analyses for HAAs cost considerably more and are also more time consuming than the THM analyses (Sérodes et al., 2003).

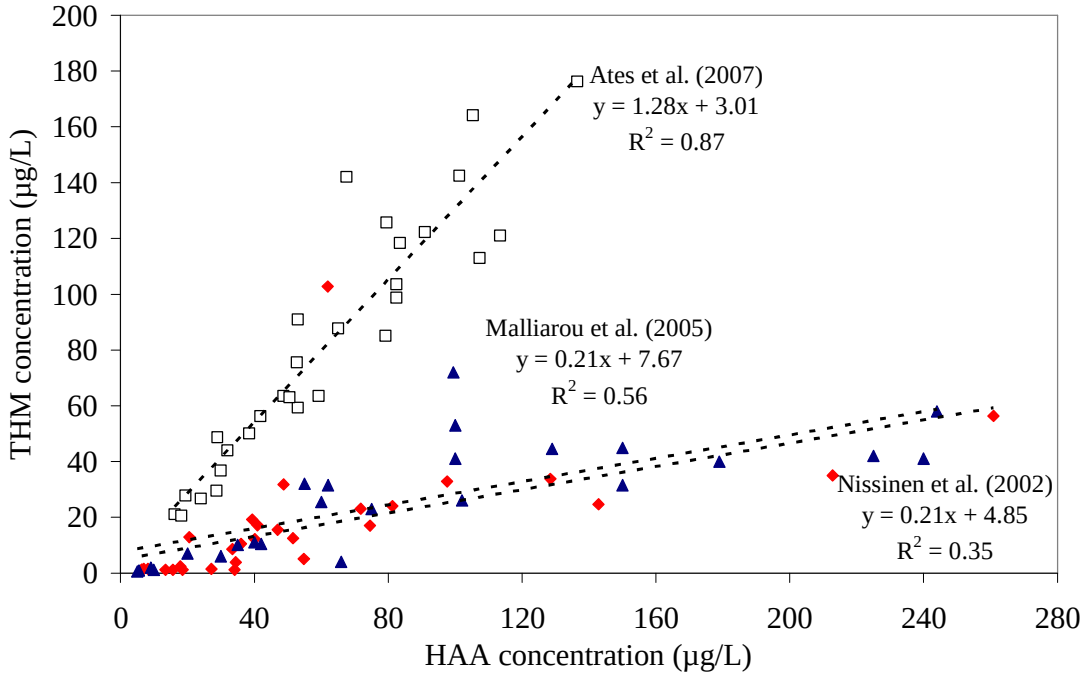



Figure 2.3 Correlation between HAAs and THMs

### 2.3.4 Influence of organic precursors

#### *2.3.4.1 Water characteristics: TOC/DOC, $UV_{254}$ and $SUVA_{254}$*

NOM consists of humic (non-polar, hydrophobic) and non-humic (polar, hydrophilic) substances, generally of terrestrial and biological origin respectively (Hwang et al., 2001). NOM provides the precursor material from which DBPs are formed; hence, the amount (described as DOC or TOC) and the nature (described as $UV_{254}$) of NOM will give some insights into the DBPs formed. SUVA (expressed in L/m-mg C) is defined as the UV absorbance (1/m) of a given sample determined at 254 nm and divided by the DOC concentration (mg/L) of the sample, and can give information on the type of NOM present in the sample. Guidelines for SUVA are shown below (Table 2.5).

Table 2.5 Guidelines for the nature of NOM (Edwald and Tobiason, 1999)

| SUVA (L/m-mg C) | Composition of the water source |
|---|---|
| > 4 | Mostly aquatic humics.<br>High hydrophobicity, high molecular weight (MW) |
| 2 - 4 | Mixture of aquatic humics and other NOM.<br>Mixture of hydrophobic and hydrophilic NOM, intermediate MW |
| < 2 | Mostly non-humics.<br>Low hydrophobicity, low MW |

TOC/DOC, $UV_{254}$ and $SUVA_{254}$ are surrogate parameters for estimating the extent of DBP formation. A review of the literature has identified a number of relationships between the water characteristics, HAAs and THMs.

First of all, data from a range of 43 drinking and treated waters from 5 references (Allgeier and Summers, 1995; Ratnaweera et al., 1999; Nokes et al., 1999; Siddiqui et al., 2000; Volk et al., 2000) and 32 raw waters from 6 references (Collins et al., 1986; Allgeier and Summers, 1995; Ratnaweera et al., 1999; Vilgé-Ritter et al., 1999; Siddiqui et al., 2000; Volk et al., 2000) were collated. A good linear relationship between the concentration of organic matter (expressed as DOC or TOC) and $UV_{254}$ was observed in drinking and treated waters with an $R^2$ of 0.96 (Figure 2.4). For comparison, the same relationship was investigated for raw waters and it was observed a similar $R^2$ (0.94), showing that the relationship is similar before and after treatment.

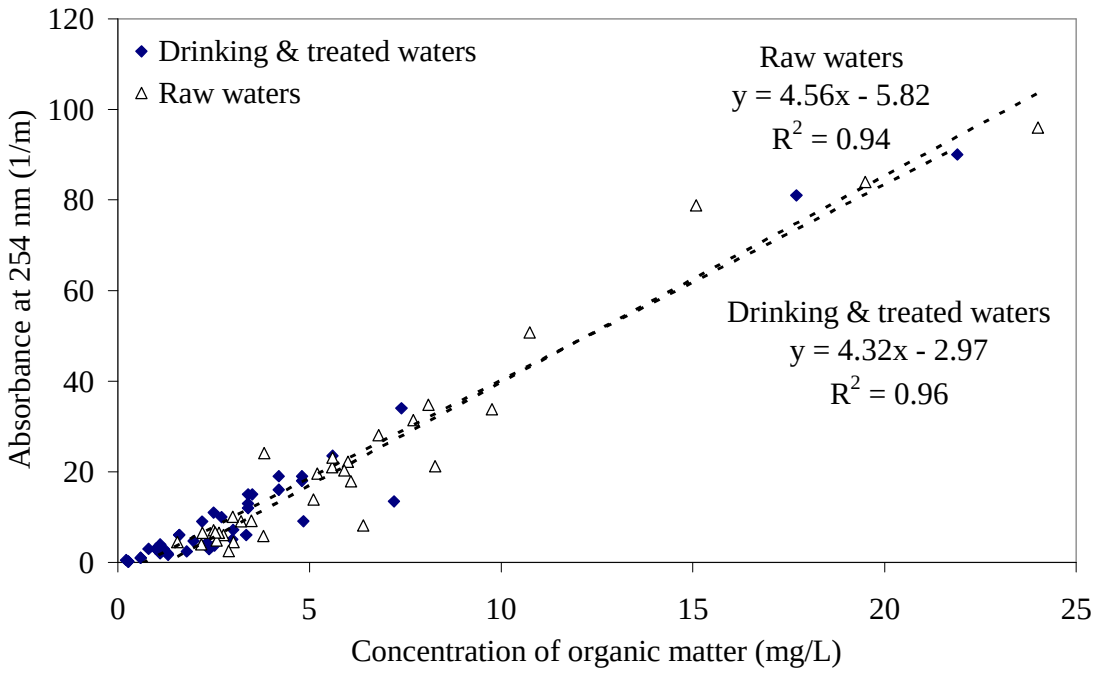



Figure 2.4 Relationship between the organic matter concentration (TOC/DOC) and $UV_{254}$ for a range of 43 drinking and treated waters and 32 raw waters

Secondly, it has been reported a linear positive relationship between HAA and THM formation potential (FP) and the water characteristics (Shorney et al., 1999; Hwang et al., 2001; White et al., 2003). The correlation between DOC and HAA-FP and THM-FP

were good, with an $R^2$ above 0.73 (Table 2.6). Ates et al. (2007) found an exponential correlation between HAAs, THMs and DOC, with an $R^2$ of 0.88 and 0.92 respectively. Although excellent correlations have been reported between DOC and DBP-FP for a single water, these correlations are not as good when waters from different sources are included, and this because waters from different sources tend to have different specific DBP yields as determined by their particular watershed characteristics (Reckhow and Singer, 1990). A Combination of good and moderate relationships was reported between DBPs and $UV_{254}$ and $SUVA_{254}$ (Table 2.6).

Table 2.6 Relationship between HAA-FP and THM-FP and water characteristics in treated waters

| | White et al. (2003) | Shorney et al. (1999) | Ates et al. (2007) | Hwang et al. (2001) |
|---|---|---|---|---|
| Number of water samples | 15 | 19 | 29 | 7 |
| $R^2$ for HAA-FP to DOC | 0.86 | 0.73 | 0.88 [a] | 0.80 |
| $R^2$ for THM-FP to DOC | 0.87 | 0.83 | 0.92 [a] | 0.97 |
| $R^2$ for HAA-FP to $UV_{254}$ | 0.99 | 0.59 | 0.91 | 0.91 |
| $R^2$ for THM-FP to $UV_{254}$ | 0.99 | 0.92 | 0.93 | 1.00 |
| $R^2$ for HAA-FP to $SUVA_{254}$ | 0.90 | 0.71 | 0.77 | NR [b] |
| $R^2$ for THM-FP to $SUVA_{254}$ | 0.91 | 0.55 | 0.69 | NR [b] |

[a] Exponential relationship; [b] Not reported.

Reckhow et al. (1990) also reported a linear positive relationship between THM-FP and $SUVA_{254}$. A linear positive relationship has also been reported for HAA-FP and $SUVA_{254}$ with higher correlations than those shown for THM-FP (Singer et al., 2002). Neither the relationship reported between both DBPs nor $SUVA_{254}$ and HAA-FP was as strong as the relationship reported between both DBPs and TOC/DOC and $UV_{254}$ separately (Singer et al., 2002).

#### *2.3.4.2 NOM fractionation*

NOM found in water consists of both hydrophobic and hydrophilic species that contribute considerably to the formation of DBPs (Goslan et al., 2002). Typically, the hydrophobic is the largest fraction of the NOM pool (Hwang et al., 2001). In order to better understand the link between precursors and DBPs, the different fractions of aquatic NOM are isolated and fractionated and then chlorinated to determine their DBP-FP. Eight fractions have been reported in the literature:

- Hydrophilic base (HPI-B): amphoteric proteinaceous materials containing amino acids, amino sugars, peptides and proteins (Leenheer, 1981),
- Hydrophilic acid (HPI-A): organic compound of the hydroxyl group (Leenheer, 1981),
- Hydrophilic neutral (HPI-N): organic compound made up of polysaccharides (Marhaba and Van, 2000),
- Colloids: consistent composition of predominantly non-reactive carbohydrates and N-acetylaminosugars (Hwang et al., 2001),
- Hydrophobic base (HPO-B): humic substance (Leenheer, 1981),
- Hydrophobic acid (HPO-A): a soil fulvic (Marhaba and Van, 2000),
- Hydrophobic neutral (HPO-N): a mix of hydrocarbon and carbonyl compounds (Leenheer, 1981),
- Transphilic (TPI): intermediate polarity, generally more hydrophobic character than hydrophilic, but it is variable and highly dependent on the particular source of the transphilic NOM (Hwang et al., 2001).

In the UK, chlorination tends to occur after the water has been treated by a coagulant and filtered (Parsons and Jefferson, 2006; Sharp et al., 2006), which is different from US treatment practices where pre-chlorination is widely used (Singer et al., 2002). After conventional treatment, NOM is mainly hydrophilic in character and low in concentration (Goslan et al., 2002). However, a review of the literature undertaken on drinking and treated waters or waters with low humic content (Table 2.7) showed that the hydrophilic NOM can contribute substantially to the formation of DBPs.

Kanokkantapong et al. (2006) found the hydrophilic neutral fraction to be the most reactive towards the formation of HAAs, whereas Marhaba and Van (2000) reported the hydrophobic neutral to be the most reactive fractions for the formation of HAAs and THMs. Sinha et al. (1997) and Goslan et al. (2002) reported the humic (hydrophobic) fraction to be very reactive in regards to the THMs. Kim and Yu (2005) found the hydrophobic and the hydrophilic fractions to give similar THM concentrations, and the

hydrophilic fraction to be the most reactive towards the formation of HAAs. Croué et al. (2000) reported similar DBP concentrations for each fraction studied.

Two studies reported levels of chlorine demand from each fraction (Table 2.7). No specific trend could be observed. Kanokkantapong et al. (2006) reported the hydrophilic neutral to be the most reactive fraction with chlorine, whereas Croué et al. (2000) found the transphilic neutral as the most active fraction.

Table 2.7 Fractions, their characteristics, their chlorine demand and their DBP-FP

| Fractions | Treatment | Distribution of DOC (%) | Chlorine demand (mg/L) | HAA detected | HAA-FP (µg/mg C) | THM-FP (µg/mg C) | Correlation with DOC ($R^2$) | Reference |
|---|---|---|---|---|---|---|---|---|
| Hydrophobic neutral | Filtered water | 5.0 – 12 | 0.61 | $HAA_5$ | 3.52 | NR [a] | 0.98 | Kanokkantapong et al. (2006) |
| Hydrophobic base | | 1.0 – 3.0 | 0.22 | | 5.72 | NR [a] | 1.00 | |
| Hydrophobic acid | | 30- 33 | 1.33 | | 15.2 | NR [a] | 1.00 | |
| Hydrophilic base | | 3.0 – 5.0 | 1.33 | | 4.72 | NR [a] | 1.00 | |
| Hydrophilic acid | | 8.0 – 19 | 0.40 | | 6.78 | NR [a] | 0.96 | |
| Hydrophilic neutral | | 31 – 41 | 3.47 | | 28.5 | NR [a] | 1.00 | |
| Humic acid | Coagulation, dissolved air flotation, rapid gravity filtration | 2.0 – 5.0 | NR [a] | NR [a] | NR [a] | 11.7 – 154 | NR [a] | Goslan et al. (2002) |
| Fulvic acid | | 14 – 33 | NR [a] | | NR [a] | 84.3 - 92.0 | NR [a] | |
| Hydrophilic acid | | 1.0 – 11 | NR [a] | | NR [a] | 11.9 - 43.9 | NR [a] | |
| Hydrophilic non acid | | 54 – 80 | NR [a] | | NR [a] | 4.00 - 70.2 | NR [a] | |
| Hydrophobic | Filtered water | 35 | NR [a] | NR [a] | 16.3 | 42.3 | NR [a] | Kim and Yu (2005) |
| Hydrophilic | | 65 | NR [a] | | 24.1 | 41.8 | NR [a] | |
| Hydrophobic neutral | Effluent water | 8.6 | NR [a] | $HAA_6$ | 2.00 | 2.00 | NR [a] | Marhaba and Van (2000) |
| Hydrophobic base | | 11 | NR [a] | | 0.60 | 0.40 | NR [a] | |
| Hydrophobic acid | | 11 | NR [a] | | 0.80 | 1.20 | NR [a] | |
| Hydrophilic base | | 11 | NR [a] | | 0.50 | 0.30 | NR [a] | |
| Hydrophilic acid | | 40 | NR [a] | | NR [a] | 10.0 | NR [a] | |
| Hydrophilic neutral | | 17 | NR [a] | | NR [a] | NR [a] | NR [a] | |
| Humic acid | Optimized coagulation | NR [a] | NR [a] | $HAA_6$ | 40.0 - 100 | 45.0 - 150 | NR [a] | Sinha et al. (1997) |
| Non-humic acid | | NR [a] | NR [a] | | 40.0 – 60.0 | 25.0 – 75.0 | NR [a] | |

| Fractions | Treatment | Distribution of DOC (%) | Chlorine demand (mg $Cl_2$/mg C) | HAA detected | HAA-FP (µg/mg) | THM-FP (µg/mg) | Correlation with DOC ($R^2$) | Reference |
|---|---|---|---|---|---|---|---|---|
| Hydrophobic acid | Filtered water | 47 | NR [a] | $HAA_5$ | 142 | 135 | NR [a] | Chang et al. (2001) |
| Hydrophobic neutral | | 30 | NR [a] | | 40.0 | 100 | NR [a] | |
| Hydrophobic base | | 16 | NR [a] | | 20.0 | 120 | NR [a] | |
| Hydrophilic | | 7.0 | NR [a] | | 120 | 60.0 | NR [a] | |
| Hydrophobic neutral | Filtered water [b] | 3.0 | 0.83 | TCAA and DCAA | 28.0 | 29.0 | NR [a] | Croué et al. (2000) |
| Hydrophobic acid | | 31 | 0.95 | | 42.0 | 46.0 | NR [a] | |
| Transphilic acid | | 14 | 0.81 | | 35.0 | 39.0 | NR [a] | |
| Transphilic neutral | | 12 | 2.30 | | 32.0 | 25.0 | NR [a] | |
| Hydrophilic acid | | | 0.86 | | 40.0 | 35.0 | NR [a] | |
| Hydrophilic neutral | | 6.0 | 1.00 | | 34.0 | 28.0 | NR [a] | |
| Hydrophobic | Ozone contractor effluent [c] | 36 | NR [a] | $HAA_9$ | 0.04 [d] | 0.07 [d] | NR [a] | Hwang et al. (2000) |
| Transphilic | | 15 | NR [a] | | 0.06 [d] | 0.09 [d] | NR [a] | |
| Hydrophilic acid+neutral | | 7.5 | NR [a] | | 0.21 [d] | 0.17 [d] | NR [a] | |
| Hydrophilic base | | 0.2 | NR [a] | | 0.17 [d] | 0.12 [d] | NR [a] | |
| Colloids | | 0.5 | NR [a] | | 0.06 [d] | 0.04 [d] | NR [a] | |

[a] Not reported; [b] DOC loss = 34%; [c] DOC loss = 41%; [d] DBP yield (µmol/µmol) expressed in percentage (%).

In their study investigating polar NOM, Hwang et al. (2001) reported the hydrophilic base to be the most reactive fractions (Table 2.8) towards chlorine and the hydrophilic acid + neutral to be the most reactive fraction in regards to the formation of HAAs and THMs. They also reported that the ratio between HAAs and THMs was different in each fraction and the DXAAs were always greater in each fraction than the TXAAs (Table 2.8). A summary of the fraction composition is also given (Table 2.8).

Table 2.8 Summary of NOM properties (Hwang et al., 2001)

| Fraction/ Parameter | Hydrophobic | Transphilic | Hydrophilic A+N [d] | Hydrophilic Base | Colloids |
|---|---|---|---|---|---|
| $Cl_2$ demand | + | + | ++ | ++++ | + |
| THM yield | +++ | +++ | ++++ | ++ | + |
| HAA yield | ++ | ++ | ++++ | variable | + |
| $HAA_9$/THMs | THMs>$HAA_9$ | THMs>$HAA_9$ | THMs~$HAA_9$ | $HAA_9$>THMs | THMs~$HAA_9$ |
| DXAA/TXAA ratio | ~1.1 | ~1.6 | ~2.4 | ~2.7 | ~2.9 |
| Molecular weight | Highest | Intermediate | Lowest | NA [a] | NA [a] |
| DBPprecursor ($^{13}C$ NMR) | Ketones Aromatic C=C Phenols | Less aromatics, Hydroxyl acids Methylenes | Hydroxy acid | NA [a] | NA [a] |
| Composition (pyrolysis) | Aromatic Phenolic | Aromatic Phenolic Proteins | Carbodydrates Aminosugars di-, tri-, mixed alcohols and acids | Proteins and aminosugars | Carbodydrates Aminosugars DNA [b], PHBs [c], fatty acids |

+ Lowest yield, ++++ highest yield (µmol DBP/µmol DOC); [a] Not analysed; [b] Deoxyribonucleic acid; [c] Polyhydroxybutyrates; [d] Hydrophilic acid + neutral.

Whilst a review of the literature showed significant contradictions in which fractions contribute the most to the DBP formation, it is true that the hydrophilic material can contribute to the formation of DBPs. Therefore, NOM, that is mainly hydrophilic in character after conventional treatment processes, should be studied for their DBP-FP (Goslan et al., 2002).

### 2.3.5 Influence of inorganic precursors: bromide

When chlorine is added to the water containing bromide, the bromide ions are oxidised to hypobromous acid as shown in Equation 2.4, and hypobromous acid reacts with NOM to form brominated DBPs. Heller-Grossman et al. (1993) and Cowman and

Singer (1996) reported that low bromide-containing waters disinfected with chlorine formed preferentially TCM, DCAA and TCAA, whereas there were a dominance of brominated DBPs in chlorinated waters containing levels of bromide > 100 µg/L. Typical concentrations of bromide in natural waters usually range from 30 to 200 µg/L, with an average of 100 µg/L (Amy et al., 1994). Hence, it is likely that most of the waters disinfected with chlorine will have the potential to form brominated DBPs.

Hua et al. (2006) observed the shift of DBP speciation towards the brominated species when adding bromide into the water sources. Indeed they reported that the total concentration of the regulated $HAA_5$ (MCAA, MBAA, DCAA, TCAA and DBAA) decreases as the bromide concentration increases because DCAA and TCAA significantly decrease and only two brominated species are measured, whereas the addition of bromide increases the total $HAA_9$ (Table 2.9). An investigation into the effect of bromide ions on HAA formation reported that bromine is more reactive than chlorine in the reactions of substitution and addition that form HAAs (Cowman and Singer, 1996). Specifically, in halogen substitution of DXAA formation, hypobromous acid is 25 times stronger than free chlorine (hypochlorous acid) (Chang et al., 2001).

Table 2.9 Effect of bromide on the molar yield of THMs and HAAs (reaction conditions: pH = 7, contact time = 48 h, temperature = 20°C, $Cl_2$ dose = 6.2 mg/L and initial water source bromide concentration = 63 µg/L) (Hua et al., 2006)

| Bromide addition (µmol/L) | DBPs (µmol/L) | | |
|---|---|---|---|
| | $HAA_5$ | $HAA_9$ | $THM_4$ |
| 0 | 0.90 | 1.05 | 1.25 |
| 2 | 0.70 | 1.10 | 1.45 |
| 10 | 0.40 | 1.25 | 1.95 |
| 30 | 0.50 | 1.40 | 2.20 |

In terms of THMs, Hua et al. (2006) reported that increasing initial bromide concentrations resulted in a substantially increase of 74% of the THM molar concentration (Table 2.9). Amy et al. (1991) found that free chlorine is a more effective oxidant, whereas hypobromous acid behaves as a more efficient halogen substitution agent in the formation of THMs. Hence, more than 50% of the bromide is incorporated into THMs compared to 5 to 10% of the chlorine. Additionally hypobromous acid attacks more sites in the THM precursors and reacts with them faster than with free chlorine (Krasner, 1999).

It should be noted that while doing FP tests, chlorine is used in excess leading to more chlorinated DBPs being formed than brominated ones (Symons et al., 1993).

### 2.3.6 Influence of water treatment variables

#### *2.3.6.1 pH*

It is well established that the formation of THMs increases with increasing pH (Singer, 1999; Kim et al., 2002; Xie, 2003) as it has been shown that the formation of THMs consists of alternate hydrolysis and halogenation steps that are enhanced at higher pH (Trussell and Umphres, 1978). However, the effect of pH on the formation of HAAs is equivocal.

Overall, HAA formation increases with decreasing pH (Krasner, 1999). Specifically, Liang and Singer (2003) reported that increasing pH from 6 to 8 had a little effect on the formation of MXAA and DXAA, but significantly decreased the formation of TXAA and in particular TCAA. DCAA, the other species the most affected by pH, was reported to be the highest at pH 7 on a pH ranges from 5.0 to 9.4 (Krasner et al., 1999).

The speciation of HAAs and THMs at different pH values is determined by the formation mechanisms of the different species. Based on Reckhow and Singer's mechanism (1985), THMs and TXAA have a common precursor structure (R-CO-$CX_3$), and the relative formation of these species is determined by the nature of the R group and pH. Under alkaline conditions, base-catalysed hydrolysis prevailed, yielding more THMs. In acidic environments, on the other hand, TXAA will be formed if the R group is a readily oxidisable functional group capable of easily donating an electron pair to the rest of the molecule. In the absence of such an oxidative cleavage (e.g., if the R group is not a readily oxidisable functional group), hydrolysis might still prevail, resulting in THMs (Singer et al., 2002). The model of Reckhow and Singer (1985) also showed that there might be more precursor structures and formation pathways for DXAA than for TXAA, which may make the formation of DXAA exhibit more complex behaviour with respect to pH (Singer et al., 2002).

#### *2.3.6.2 Temperature*

The temperature has been previously correlated with HAAs by Dojlido et al. (1999), who reported that during the winter season (1°C) the level of HAAs was 0.63 µg/mg C, whereas during the summer (23°C), concentration reached 7.4 µg/mg C. In a study by Malliarou et al. (2005), temperature was significantly correlated with the ratio of total THM and total HAA.

However, the effect of temperature (rise from 0 to 33°C) on the THM yield was rather limited (El-Dib and Ali, 1995). Specifically, Carlson and Hardy (1998) found that THMs were impacted by the temperature, but this at longer contact time.

It is thought that the nature of NOM may also differ from summer to winter and could be responsible for the difference of DBP concentration measured.

#### *2.3.6.3 Alternative disinfectants*

As HAAs and THMs are formed by the reaction of NOM with chlorine, methods of control include the use of alternative disinfectants, such as chloramines.

Chloramines include monochloramine ($NH_2Cl$), dichloramine ($NHCl_2$) and trichloramine ($NCl_3$) (Section 2.2.2). However, monochloramine is the predominant chloramine species present under the controlled conditions typically found in water treatment works and distribution systems (Vikesland et al., 1998). Many utilities have switched to monochloramine as a secondary disinfectant because it generally results in lower concentrations of THMs and HAAs (Speitel, 1999; Diehl et al., 2000). With concurrent addition of chlorine and ammonia, the HAA formation is typically 5 to 20% of that observed with chlorine alone (Speitel, 1999) and DXAAs are the most commonly formed DBPs comprising > 90% of the total HAA (Diehl et al., 2000). Many plants have a significant period of exposure to free chlorine before ammonia addition for purpose of meeting CT requirements (Section 2.2.2) (Seidel et al., 2000). This prechlorination period, necessitated by disinfection regulation, is of greatest concern when DBP formation is considered as it gives free chlorine the opportunity to react with NOM. Clearly, by adding free chorine first rather than adding monochloramine, more HAAs and THMs are formed. Pope et al. (2006) looked at the effect of prechlorination

and concluded that during short periods of prechlorination (5 or 20 minutes), significantly more DXAA formation, as well as MXAA and TXAA, occurred, relative to the period of free chlorination. In one of their waters studied (Pope et al., 2006), the use of preformed chloramines resulted in 9 µg/L of DXAA after 48 hours incubation, whereas prechlorination for 5 and 20 minutes formed 25 and 35 µg/L of DXAA respectively. The effect of pH and $Cl_2$:N ratio impacts also the formation of DBPs, and by increasing the $Cl_2$:N ratio and decreasing the pH, HAA formation will be maximised (Diehl et al., 2000). For example, Diehl et al. (2000) reported that a pH of 6 and a $Cl_2$:N ratio of 7:1 resulted in about 19 µg/L of HAAs formed, whereas in the same water, at a pH 10 and a $Cl_2$:N ratio of 3:1, less than 5 µg/L of HAAs were formed.

When monochloramine reacts with NOM to form DBPs, the DBP formation pathways remain unclear. When bromide is absent, monochloramine and its two decomposition products, free chlorine and dichloramine potentially react with NOM to form HAAs (Karanfil et al., 2008). Hong et al. (2007) and Karanfil et al. (2007) showed that the direct reaction between monochloramine and NOM plays the major role and is responsible for about 80% of HAA formation and that the remaining HAA formation was attributed to free chlorine that results from monochloramine decomposition. No HAA formation was attributed to dichloramine. Whilst Duirk et al. (2005) and Duirk and Valentine (2006) concluded that DXAA formation was most due to the direct reaction of free chlorine, in quasi-equilibrium with monochloramine, with NOM; a schematic showing the pathways are presented below (Figure 2.5).

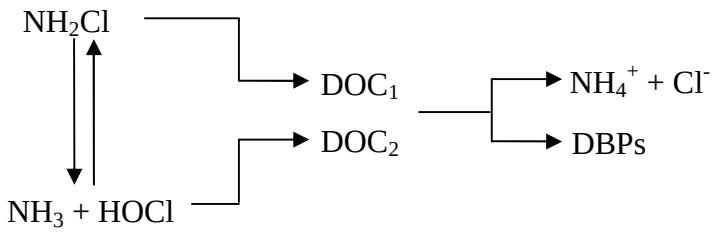



Figure 2.5 Schematic of monochloramine reaction pathways in the presence of NOM (as DOC). Monochloramine reacts directly with reactive site concentration [$DOC_1$], and free chlorine with reactive site concentration [$DOC_2$]. Adapted from Duirk and Valentine (2006)

The presence of bromide significantly complicates the chemistry (Diehl et al., 2000; Karanfil et al., 2007). Bromamines, chloramines and bromochloramine would co-exist in a chloraminated samples and Pope et al. (2006) found that the dihalogenated bromine-substituted species (BCAA and DBAA) formed more rapidly than the DCAA because bromochloramine has a higher reactivity than monochloramine (Vikesland et al., 2001).

Other alternative disinfectants include ozonation and chlorine dioxide. Ozonation is used in the UK as a pre-treatment but is usually associated to the formation of bromate (Jarvis et al., 2007). Although chlorine dioxide is used in the US, this is not the case in the UK because of the chlorite/chlorate by products associated to its use. DWI (2009) states the level of chlorine dioxide, chlorate and chlorite permitted in drinking water to be 0.5 µg/mL in total.

#### *2.3.6.4 Disinfectant dose*

Increasing the chlorine dose results in increased DBP formation up to a point where the concentrations reached an equilibrium (Fleischacker and Randtke, 1983; Carlson and Hardy, 1998). Fleischacker and Randtke (1983) stated that after 96 hours contact time, a dose less than 6 mg free chlorine per mg DOC, THMs form in proportion to increasing free chlorine, whereas at a dose greater than 6 mg free chlorine per mg DOC, little additional THMs form as free chlorine increases. Carlson and Hardy (1998) also found that the point at which the reaction was no longer chlorine limited was 1 mg free chlorine per mg of TOC; this evaluated at a shorter contact time (< 7 hours). However, it is thought that the nature of NOM in the water will also have an effect on the point at which the reaction is no longer chlorine limited. Similar patterns were also observed for HAAs.

#### *2.3.6.5 Reaction time and kinetics*

The effect of the reaction time has been widely studied with the common statement that HAAs and THMs were formed rapidly in the first few hours of the reaction and then the formation slowed as the concentrations of the reactants (either NOM or chlorine) decreased with time (Reckhow et al., 1990; Singer, 1999; Gallard and Von Gunten, 2002; Singer et al., 2002; Liang and Singer, 2003; Nikolaou et al., 2004).

From this finding, the fast rate of reaction has been referred to as a first order reaction and the slower rate, second order. The reactions and the calculation of the rate are shown below:

$1^{st}\ \text{Order}: A + B \rightarrow C$

$$\text{Rate} = k_1[A]^1[B]^1 = k[A][B], \qquad \text{Equation 2.8}$$

$2^{nd}\ \text{Order}: A + 2B \rightarrow C$

$$\text{Rate} = k_2[A]^1[B]^2 = k[A][B]^2, \qquad \text{Equation 2.9}$$

where $k_1$ and $k_2$ are the constant of $1^{st}$ and $2^{nd}$ order respectively, A and B are reactants (NOM and disinfectant) and C is the products (DBPs) (Chowdhury and Amy, 1999).

### 2.3.7 Predictive models for HAAs and THMs

Many models have been developed to predict THM and HAA formation (Amy et al., 1987; Adin et al., 1991; Lou and Chiang, 1994; Chang et al., 1996; Rathbun, 1996; Garcia-Villanova et al., 1997; Clark, 1998; Chowdhury et al. 1999; Rodriguez et al., 2000; Golfinopoulos and Arhonditsis, 2002; Gang et al., 2003). The creation of predictive models requires a large database of existing results. Two studies carried out by Sohn et al. (2004) and Sadiq and Rodriguez (2004) reviewed the existing models for the prediction of DBPs in raw, drinking and treated water. The review by Sohn et al., (2004) focused on several types of models, such as empirical power function and empirical kinetic models, in order to find more about the robustness and the accuracy for the DBP prediction. What has been concluded from these reviews is the greater amount of models available for THMs in comparison with those available for HAAs. Only 22% of the models reviewed by Sadiq and Rodriguez (2004) are related to HAAs. A summary of selective predictive HAA models for application in raw and treated waters are presented (Table 2.10). The HAA models identified in this summary are of

the form: DOC/UV based models (Watson, 1993; Amy et al., 1998; Sohn et al., 2004), chlorine demand models (Gang et al., 2002; Gang et al., 2003) and linear regression models (Villanueva et al, 2003; Sérodes et al., 2003).

Table 2.10 Selected HAA predictive models

| Species (µg/L) | Predictive models for HAA | $R^2$ | Water source | Advantages | Limitations | Reference |
|---|---|---|---|---|---|---|
| MCAA | $1.634\ (TOC)^{0.753}\ (Br^- + 0.01)^{-0.085}\ (pH)^{-1.124}\ (Cl_2)^{0.509}\ (t)^{0.300}$ | 0.82 | Not real water | Use of independent databases for model validation | The water quality and the chlorination conditions do not represent situations encountered in real water utilities | Watson (1993) |
| DCAA | $0.605\ (TOC)^{0.291}\ (UV)^{0.726}\ (Br^- + 0.01)^{-0.568}\ (Cl_2)^{0.48}\ (t)^{0.239}\ (T)^{0.665}$ | 0.97 | | | | |
| TCAA | $87.182\ (TOC)^{0.355}\ (UV)^{0.901}\ (Br^- + 0.01)^{0.679}\ (pH)^{1.732}\ (Cl_2)^{0.881}\ (t)^{0.264}$ | 0.98 | | | | |
| MBAA | $0.176\ (TOC)^{1.664}\ (UV)^{-0.624}\ (Br^-)^{0.795}\ (pH)^{-0.927}\ (t)^{0.145}\ (T)^{0.45}$ | 0.8 | | | | |
| DBAA | $84.945\ (TOC)^{-0.62}\ (UV)^{0.651}\ (Br^-)^{1.073}\ (Cl_2)^{-0.2}\ (t)^{0.12}\ (T)^{0.657}$ | 0.95 | | | | |
| HAAs | Linear regression in function of various THM species | 0.57 – 0.97 | NR [a] | Data and models have potential applications for exposure assessment in epidemiological studies | Models do not consider chlorine dose, temperature, etc. | Villanueva et al. (2003) |
| HAAs | Single linear and non-linear regression models for water of single utility | 0.56 – 0.92 | NR [a] | Can represent the real seasonal variations of environmental and water quality characteristics | Variation according to the DBP species to be modelled and to the utility | Sérodes et al. (2003) |

| Species (µg/L) | Predictive models for HAA | $R^2$ | Water source | Advantages | Limitations | Reference |
|---|---|---|---|---|---|---|
| $HAA_6$ | DOC-based model<br>$HAA_6 = 9.98\ (DOC)^{0.935}\ (Cl_2)^{0.443}\ (Br^-)^{-0.031}\ (T)^{0.387}\ (pH)^{-0.655}\ (t)^{0.178}$ | 0.87 | Raw water | Strength of the model: flexibility and applicability. | To a various water quality as well as different operating conditions | Amy et al. (1998) |
| $HAA_6$ | UV-based models<br>$HAA_6 = 171.4\ (UV)^{0.584}\ (Cl_2)^{0.398}\ (Br^-)^{-0.091}\ (T)^{0.396}\ (pH)^{-0.645}\ (t)^{0.178}$ | 0.80 | Raw water | | | Sohn et al. (2004) |
| $HAA_6$ | DOC*UV-based models<br>$HAA_6 = 101.2\ (DOC*UV)^{0.452}\ (Cl_2)^{0.194}\ (Br^-)^{-0.0698}\ (T)^{0.346}\ (pH)^{-0.623}\ (t)^{0.180}$ | 0.85 | Raw water | | | Sohn et al. (2004) |
| $HAA_6$ | DOC-based model<br>$HAA_6 = 5.22\ (DOC)^{0.585}\ (Cl_2)^{0.565}\ (Br^-)^{-0.031}\ (t)^{0.153}$ | 0.92 | Coagulated water (alum or iron) | Simplicity, flexibility and applicability | Do not take into account pH and temperature. Use of another equation for correction | Amy et al. (1998) |
| $HAA_6$ | UV-based models (developed from EPA 1998 database)<br>$HAA_6 = 63.7\ (UV)^{0.419}\ (Cl_2)^{0.640}\ (Br^-)^{-0.066}\ (t)^{0.161}$ | 0.92 | Coagulated water (alum or iron) | Simplicity, flexibility and applicability | Do not take into account pH and temperature. Use of another equation for correction | Sohn et al. (2004) |
| $HAA_6$ | DOC*UV-based models (developed from EPA 1998 database)<br>$HAA_6 = 30.7\ (DOC*UV)^{0.302}\ (Cl_2)^{0.541}\ (BR^-)^{-0.012}\ (t)^{0.161}$ | 0.94 | Coagulated water (alum or iron) | Simplicity, flexibility and applicability | Do not take into account pH and temperature. Use of another equation for correction | Sohn et al. (2004) |

| Species (µg/L) | Predictive models for HAA | $R^2$ | Water source | Advantages | Limitations | Reference |
|---|---|---|---|---|---|---|
| $HAA_6$ | pH and temperature correction<br>$HAA_6 = (HAA_{6@pH = 7.5, T = 20°C})*(0.932)^{(pH-7.5)}\ (1.021)^{(T-20)}$ | 0.85 | Coagulated water (alum or iron) | This equation modify the existing coagulated water DBP models, so that there are applicable under different pH and temperature | Temperature and pH correction factors applicable in coagulated waters only | Sohn et al. (2004) |
| $HAA_5$ | $4.8 * 10^4\ [OH^-]^{0.35}\ (C_0(1\text{-}\exp(\text{-}kt))^{0.43})(UV_{254})^{0.34}$ | 0.74 | Raw water | Include temperature, pH, chlorine dosage and $UV_{254}$ absorbance | Concentration of $[OH^-]$ calculated from the raw water pH and temperature | Sung et al. (2000) |
| $HAA_9$ | Model based on chlorine demand<br>$HAA_9 = ßC_0\ \{1\text{-}fe^{-kR*t} - (1\text{-}f)e^{-kS*t}\}$ | 0.98 | From raw to treated water | The model can be applied accurately from raw to alum treated water | The model may not perform well if tested outside the typical conditions (pH 8.0 ± 0.2, temperature = 25°C and chlorine residual = 1.0 ± 0.5 mg/L) | Gang et al. (2002) |

TOC/DOC = concentration of NOM (mg/L); $Br^-$ = bromide ion (µg/L); $Cl_2$ = chlorine dose (mg/L); *t* = time in hours; UV = UV absorbance at 254 nm (1/cm); T = Temperature (°C); ß = $HAA_9$ yield coefficient, defined as the ratio of the concentration (µg/L)of $HAA_9$ formed to the concentration of chlorine consumed (mg/L); $C_0$ = initial chlorine concentration (mg/L); f = fraction of the chlorine demand attributed to rapid reactions; $k_R$ and $k_S$ = the first order rate constants for rapid and slow reactions respectively; [a] Not reported.

*Evaluation of models*

DOC-, UV- and DOC*UV-based models have been evaluated for their accuracy with data available in the literature. These models have been chosen because they are the only models that could fit a large database of existing results. Moreover, because this study focused on treated water, it was decided to evaluate specific models that fit this type of water. For comparison, models were also evaluated for raw water. The models are:

Amy et al. (1998):

- DOC-based model in raw water

  $HAA_6 = 9.98\ (DOC)^{0.935}\ (Cl_2)^{0.443}\ (Br^-)^{-0.031}\ (T)^{0.387}\ (pH)^{-0.655}\ (t)^{0.178}$

- DOC-based model in coagulated water (alum or iron)

  $HAA_6 = 5.22\ (DOC)^{0.585}\ (Cl_2)^{0.565}\ (Br^-)^{-0.031}\ (t)^{0.153}$

Sohn et al. (2004):

- UV-based models in raw water

  $HAA_6 = 171.4\ (UV)^{0.584}\ (Cl_2)^{0.398}\ (Br^-)^{-0.091}\ (T)^{0.396}\ (pH)^{-0.645}\ (t)^{0.178}$

- UV-based models in coagulated water (alum or iron)

  $HAA_6 = 63.7\ (UV)^{0.419}\ (Cl_2)^{0.640}\ (Br^-)^{-0.066}\ (t)^{0.161}$

Sohn et al. (2004):

- DOC*UV-based models in raw water

  $HAA_6 = 101.2\ (DOC*UV)^{0.452}\ (Cl_2)^{0.194}\ (Br^-)^{-0.0698}\ (T)^{0.346}\ (pH)^{-0.623}\ (t)^{0.180}$

- DOC*UV-based models in coagulated water (alum or iron)

  $HAA_6 = 30.7\ (DOC*UV)^{0.302}\ (Cl_2)^{0.541}\ (BR^-)^{-0.012}\ (t)^{0.161}$

In the treated water (coagulated), the temperature and pH are not considered; therefore, the correction factor (Table 2.10) was applied.

The observed HAA concentrations have been fitted against the predicted HAA concentrations, obtained using the models cited above, in raw and treated waters (Figure 2.6 A+B). Overall results show that the predicted HAA concentrations follow the same pattern than the observed ones, with more HAA predicted, when there were more HAA observed. However, in some sources, such as S1 and S7, a difference of more than 1000 µg/L could be observed in raw water, and a difference of more than 200 µg/L in S4, treated water. The greatest inaccuracy has been observed in water with the highest level of HAA observed. Therefore, it is believed that these major differences are due to important parameters such as DOC or UV that remain low for a high HAA formation. The general trend of these models was to under-estimate the formation of HAAs in both raw and treated waters. Overall, it seems that, as yet, it is not possible to accurately predict HAA concentrations with a universal model. The models tested would work better for certain water sources than for others.

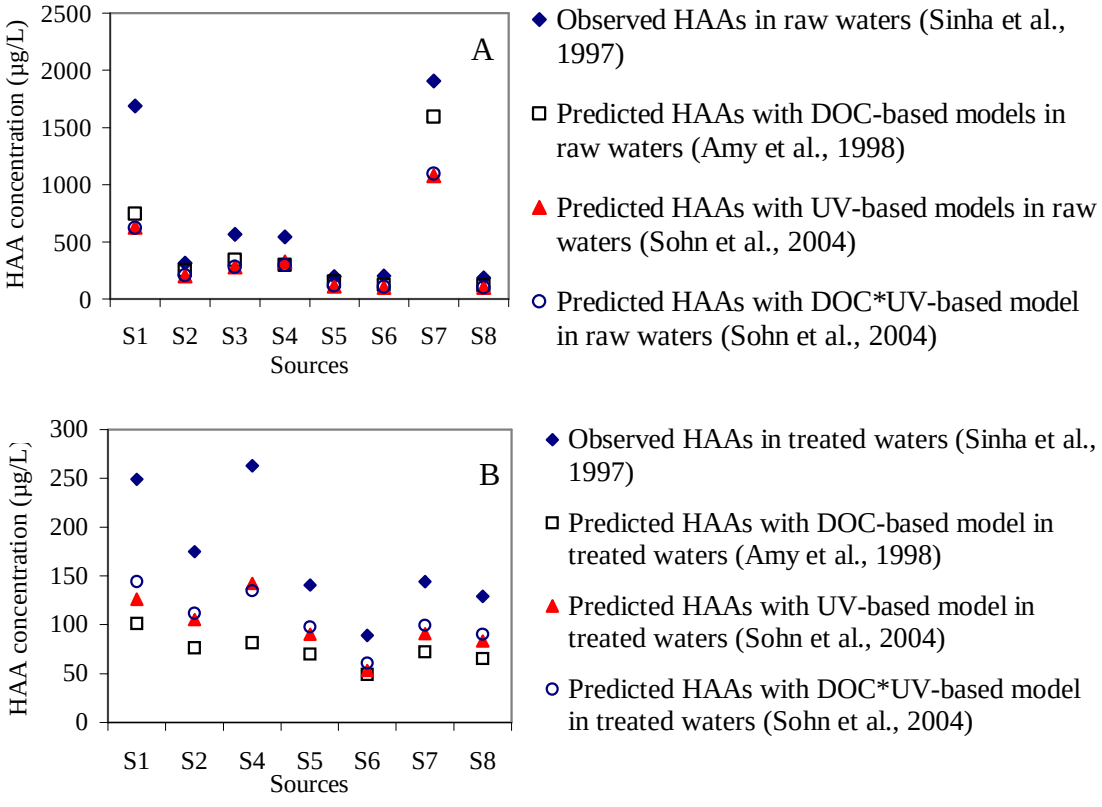



Figure 2.6 Observed HAAs against predicted HAAs using the models of Amy et al. (1998) and Sohn et al. (2004) in raw (A) and treated waters (B)

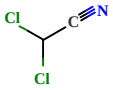
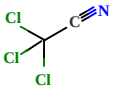
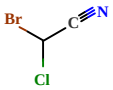
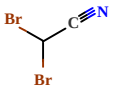
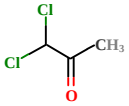
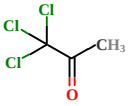
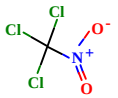
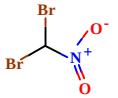
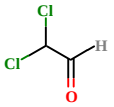
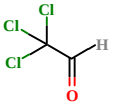
As a conclusion, scientists have to bear in mind that developing effective and accurate predictive models for both THMs and HAAs, as well as the rest of the DBPs will allow a decrease of DBPs measurement studies that require extensive experimental procedures and chromatographic analysis, which is time and cost consuming. However, developing accurate model is a complicated and difficult task that requires a considerably large database (Clark et al., 2001).

## 2.4 SEMI-VOLATILE DBP OCCURRENCE AND FORMATION FROM DRINKING WATER

While $THM_4$ are currently measured and regulated in UK waters and HAAs are considered for regulation, the literature reports more than 600 to 700 DBPs for the most common disinfectants used (chlorine, chloramines, chlorine dioxide and ozone) (Richardson et al., 1998; Krasner et al., 2006). Amongst those, 50 DBPs have been reported as high priority for potential toxicity (Krasner et al., 2001). These DBPs include i-THMs, HANs, HAs, HKs, HNMs, haloacids, haloamides, MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone] and its analogues, and N-nitrosodimethylamine (NDMA) (Mitch and Sedlak, 2002; Richardson et al., 2002; Weinberg et al., 2002; Richardson, 2003; Krasner et al., 2006).

This literature review will focus on i-THMs, HANs, HAs, HKs and HNMs, because they are the most common detected in drinking water; they will be referred as semi-volatile DBPs. The DBPs that will be further extensively studied in this study are presented below with their molecular formula, their molecular weight, their structure, their boiling point and their CAS number (Table 2.11).

Table 2.11 Chemical and physical properties of selected semi-volatile DBPs

| Semi-volatile DBP | Molecular formula | Molecular weight (g/mol) | Structure | Boiling point (°C) | CAS number |
|---|---|---|---|---|---|
| **Haloacetonitriles** | | | | | |
| DCAN | $C_2HCl_2N$ | 109.94 |  | 110-112 | 3018-12-0 |
| TCAN | $C_2Cl_3N$ | 144.39 |  | 83-84 | 545-06-2 |
| BCAN | $C_2HBrClN$ | 154.39 |  | NR[a] | 83463-62-1 |
| DBAN | $C_2HBr_2N$ | 198.84 |  | NR[a] | 3252-43-5 |
| **Haloketones** | | | | | |
| 1,1-DCP | $C_3H_4Cl_2O$ | 126.96 |  | 117 - 118 | 513-88-2 |
| 1,1,1-TCP | $C_3H_3Cl_3O$ | 161.41 |  | NR[a] | 918-00-3 |
| **Halonitromethanes** | | | | | |
| TCNM (also called chloropicrin) | $CCl_3NO_2$ | 164.38 |  | 112 | 76-06-2 |
| DBNM | $CHBr_2NO_2$ | 218.83 |  | NR[a] | 598-91-4 |
| **Haloaldehydes** | | | | | |
| DCA | $C_2H_2Cl_2O$ | 112.94 |  | 88 | 79-02-7 |
| TCA (also called chloral hydrate) | $C_2HCl_3O$ | 147.39 |  | 98 | 75-87-6 |
| **Iodo-Trihalomethanes** | | | | | |
| DCIM | $CHCl_2I$ | 210.83 |  | NR[a] | 594-04-7 |
| BCIM | $CHBrClI$ | 255.28 |  | NR[a] | 34970-00-8 |

[a]Not reported.

### 2.4.1 Toxicity and regulations

Many of the semi-volatile DBPs, discovered more recently than THMs and HAAs, were rated high priority, because they showed a potential toxicity (Richardson, 1998; Krasner et al., 2001; Plewa et al., 2004). Within the group of halogenated alkanes, such as THMs and i-THMs, the brominated and the iodinated species are of greater concern than their chlorinated counterparts, because iodine and bromine are better leaving groups than chlorine due to their greater polarisable bondings (Woo et al., 2002). Plewa et al. (2008) compared the level of cytotoxicity and genotoxicity of individual and group DBPs with CHO cells and concluded that the order of cytotoxicity and genotoxicity were iodo-DBPs > bromo-DBPs > chloro-DBPs (Figure 2.7). They also reported that HNMs and HANs were more cytotoxic and genotoxic than HAAs and THMs (Figure 2.7). For example, DCAA was reported 27 times more concentrated than DCNM, but the toxicity of DCNM was 30.8 times the one of DCAA (Plewa et al., 2004). Other chemicals to be of health concerns are the group of HKs, because 1,1-DCP and 1,1,1-TCP have shown to exert carcinogenic and mutagenic effect in mice (Bull and Robinson, 1986).

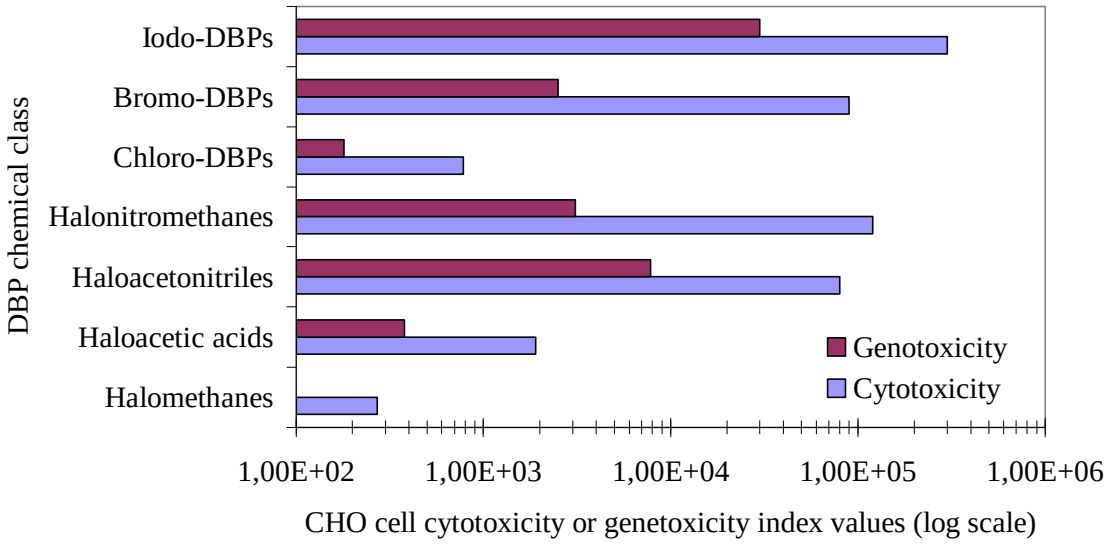



Figure 2.7 Cytotoxicity and genetoxicity indices for different classes of DBPs and for chloro-, bromo- and iodo-DBPs (Plewa et al., 2008)

Despite their potential health effects, there is no UK or US regulatory limit for these compounds, but the WHO has suggested guideline values of 20 µg/L for DCAN, 70 µg/L for DBAN and 10 µg/L for TCA (WHO, 2006).

### 2.4.2 Analytical measurement

Currently, there is one GC/ECD US EPA approved method: the US EPA Method 551.1 (1995a), which enables the measurement of 8 semi-volatile DBPs (DCAN, TCAN, BCAN, DBAN, TCA, TCNM, 1,1-DCP and 1,1,1-TCP), the four THMs, 8 chlorinated solvents and 17 pesticides/herbicides. The DBPs are extracted with LLE from water samples using MtBE and analysed using GC/ECD. The advantages of this method are the short time required for sample preparation (10 minutes) and the short run time to process the 4 THMs and the 8 semi-volatile DBPs (less than 30 minutes). On the other hand, the number of semi-volatile compounds analysed with the US EPA Method 551.1 is limited. Studies on emerging semi-volatile DBPs have therefore focused on synthesised standards that were not previously commercially available and developed new methods that incorporate approximately 50 compounds (Gonzalez et al., 2000; Krasner et al., 2001; Weinberg et al., 2002). These methods assessed, include modified versions of the LLE – GC/ECD US EPA Method 551.1 (1995a), a solid phase extraction (SPE) – GC/MS to have MS confirmation of the semi-volatile DBPs (Krasner et al., 2001). Weinberg et al. (2002) also used a purge-and-trap (P&T) – GC/MS for certain volatile chemicals. Amongst these methods, the LLE has the best extraction efficiency (Chinn et al., 2007). All these methods have been shown suitable to detect the semi-volatile DBPs in drinking water. Nevertheless, before extraction, two preservative parameters need to be controlled to avoid any DBP degradation: the quenching agent and the pH (Chinn et al., 2007). Chinn et al. (2007) showed that many of the DBPs were stable in ascorbic acid (quenching agent), but others, such as tribromoacetonitrile or tribromonitromethane degraded over time in ascorbic acid, and therefore ammonium chloride was recommended instead. Also, it has been shown that TCAN can undergo base-catalysed hydrolysis at pH higher than 5.5 (Croué and Reckhow, 1989), hence, waters with pH higher than 5.5 may present low amount of TCAN.

### 2.4.3 Typical levels in drinking water

A broad screen of the published works revealed that the concentration of most of the compounds did not exceed 10 µg/L individually (Table 2.12), the exception being TCA and DCA (Krasner et al. 2006). The HA group represents the third major class of halogenated DBPs in weight basis after the THMs and the HAAs (Krasner et al., 2001). Treatment applied played an important role on the formation of the DBPs. For example, Bichsel and Von Gunten (2000) reported that i-THMs are favoured by chloramines. Moreover, HNMs have been reported to be in higher concentration in waters pre-ozonated (Hoigné and Bader, 1998; Richardson et al., 1999).

Table 2.12 Typical levels of semi-volatile DBPs found in drinking water

| DBPs | Treatment applied | Level observed (µg/L) | Reference |
|---|---|---|---|
| DCIM | Chloramines | 0.30 | Krasner et al. (2001) |
| BCIM | | 0.20 | |
| DCIM | Chlorine | 0.50 | |
| BCIM | | 0.60 | |
| DBIM | | 0.60 | |
| Sum of DCIM, BCIM, DBIM, CDIM, BDIM and TIM | Chlorine and ammonia simultaneously | 19.0 | Krasner et al. (2006) |
| DCIM, BCIM, DBIM | Chloramines | < 1.00 | Cancho et al. (2000) |
| DCAN | Chlorine dioxide, chlorine and chloramines | 0.10 – 5.00 | Krasner et al. (2001) |
| DBAN | Chlorine and chloramines | 0.10 – 3.00 | Weinberg et al. (2002) |
| TCAN | Chlorine | 0.10 | |
| Sum HANs | Chlorine | 10.3 – 33.6 | Kim et al. (2002) |
| 1,1-DCP | Ozone and chlorine | ND[a] – 2.00 | Krasner et al. (2001) |
| 1,1,1-TCP | | ND[a] – 5.00 | |
| TCA | Chlorine and chloramines | 13.0 | Krasner et al. (2001) |
| | Ozone and chloramines | 0.30 | |
| DCA | Chlorine and chloramines | 3.00 | |
| | Ozone and chloramines | 12.0 | |
| TCNM | Chlorine dioxide, chloramines | 2.00 | Krasner et al. (2006) |
| Sum HNMs | | 10.0 | |

[a] Not detected.

### 2.4.4 Parameters affecting semi-volatile DBP formation

Until now, few studies have focused on the impact of precursors on the semi-volatile DBP formation. However, the first results stated that organic and inorganic precursors can alter the formation of DBPs. Lee et al. (2007) investigated the impact of dissolved organic nitrogen (DON) and concluded that DON can serve as a precursor material for the nitrogen-containing DBPs such as DCAN and TCNM. Bromide and iodide are also closely related to the formation of bromine and iodine-containing DBPs. Waters with high level of bromide (≥ 500 µg/L) formed more brominated HANs (BCAN and DBAN) than DCAN, and increasing the level of bromide decreased the formation of chlorinated DBPs, such as 1,1-DCP (Peters et al., 1990; Yang et al., 2007). Recently, Goslan et al. (2009) concluded that the concentration of i-THMs typically increases with increasing iodine level.

Water treatment variables can also influence the formation of the semi-volatile DBPs. Previously, the pH has been reported to be responsible of base-catalysed hydrolysis of TCAN (Section 2.4.2). The choice of disinfectants also affects the level of DBPs (Section 2.4.3). Recently, Yang et al. (2007) showed that DCAN and 1,1-DCP increased with increasing reaction time; 90% of 1,1-DCP and over 60% of DCAN being formed within seven hours and three days respectively, compared to their formation after seven days. The same study also reported that DCAN and 1,1-DCP increased with higher monochloramine doses and that the temperature did not alter the formation of DCAN and 1,1-DCP.

## 2.5 CHAPTER SUMMARY

- Several analytical methods have been reported in the literature for the measurement of HAAs. Nevertheless, few of them are suitable for the quantification of low µg/L level, expected in drinking water.
- Regarding toxicity of DBPs, work is ongoing to assess the risks to humans. It is thought that bromine-, iodine-containing DBPs pose more risk to health. Semi-volatile DBPs, such as HNMs, or HANs, are more cytotoxic and genetoxic than HAAs and THMs.

- Typical levels of HAAs in drinking water ranged from 0 to 244 µg/L (total HAA), and semi-volatile DBPs (i-THMs, HANs, HNMs, HAs, HKs) between 0 and 13 µg/L (individual species), with the highest concentration for HA, which is therefore the third prevalent group of DBPs after the HAA and the THM.
- Some studies reported that the hydrophilic NOM contributes substantially to the formation of DBPs. However, other studies contradict this statement. DBP precursors vary from one source to another and this explains why no specific trend could be identified.
- Strong and weak linear correlations have been observed between HAAs, THMs and water characteristic parameters.
- Formation of HAA will be maximised with a high DOC concentration, a high bromide concentration, a high SUVA value and a high temperature coupled with a high chlorine dose for a long contact time. HAA and THM formation will be maximise with a low and high pH respectively.
- In general, bromide and iodide, naturally present in drinking water source, enhance the formation of bromide and iodide-containing DBPs.
- The use of monochloramine, as an alternative disinfectant, has been found to minimise the formation of HAAs and THMs, provided the conditions are correct (a high pH with a low $Cl_2$:N ratio). The formation mechanism between monochloramine and NOM to form DBPs remains uncertain.
- Predictive models for the formation of HAAs under-estimate the observed level of HAAs. Developing accurate model is a complicated and difficult task that requires a considerably larger body of data and has to be water specific.

# Chapter 3

# ANALYTICAL METHODOLOGY FOR HAAs

## 3.1 INTRODUCTION

Disinfection is well known to be effective in preventing waterborne disease, but the reaction between chemical disinfectants and naturally occurring organic matter can form DBPs of potential health concern (Christman et al., 1983). A great deal is known about THM, but much less on HAA, often the second most prevalent group of DBPs formed during chlorination (Singer, 2002) (see Chapter 2). Nine species of HAAs are found in chlorinated water: MCAA, MBAA, DCAA, BCAA, TCAA, DBAA, BDCAA, DBCAA and TBAA, and, of these, five are regulated in the US. The five HAAs, MCAA, MBAA, DCAA, DBAA and TCAA, are regulated under the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR) with a maximum contaminant level of 60 µg/L (US EPA, 1998). In the UK, no regulation has been set and only one study has reported levels of HAAs in UK waters (Malliarou et al., 2005). They found concentrations that were significantly above the US EPA regulatory limits.

To monitor HAAs in drinking water, several analytical methods can be used, including GC/ECD, GC/MS, HPLC, CE and IC, where the GC methods are the most widely applied. Currently, there are four GC/ECD US EPA approved methods: the US EPA Method 552.1 (1992), US EPA Method 552.2 (1995), US EPA Method 552.3 (2003) and the Standard Method 6251 (APHA, 1998). In these methods, HAAs are extracted from water samples using either MtBE or anion exchange resins, and then converted to their methyl esters using diazomethane or acidic methanol. Several shortcomings of the three oldest methods (US EPA 1992, 1995; APHA, 1998) have been reported (Xie, 2001). Reduced susceptibility to chromatographic interferences and shorter run times were observed with GC/MS (Xie, 2001), but the MS detection significantly increases the price of analysis (Liu and Mou, 2003). In general, GC methods involve labour-intensive extraction procedures and the use of toxic derivatisation reagents, but they are typically reliable and accurate with detection limits for the nine HAAs in the low µg/L

range. HPLC, which is a method faster than GC method, can also be used for the determination of HAAs, but its detection limits are above 30 µg/L (Carrero and Rusling, 1999). CE is a suitable alternative to the chromatographic methods and has the advantages of high separation efficiency, short analysis time and minimal sample preparation (Xie and Romano, 1997; Xie et al., 2000). However, the drawback of CE is its current detection limit that allows detection only in the mg/L range (Kim et al., 2001; McRae et al., 2004). The IC method has been investigated by Nair et al. (1994) and Liu and Mou (2003) and again the method is quick with limited sample preparation. Liu and Mou (2003) reported detection limits for the nine HAAs between 0.37 and 31.64 µg/L. More details on analytical measurement are described in Chapter 2, Section 2.3.2.

For this project, a convenient and sensitive method for the direct determination of HAAs was required. Given the advantages and drawbacks for each analytical method, the choice was not straightforward. The aims of this chapter are to compare four analytical methods and to validate the most suitable one for the measurement of HAAs. Here, a suitable method is regarded as one that has a minimum reporting level (MRL) of 0.5 µg/L (lowest continuing calibration standard) and therefore a detection limit of 0.17 µg/L for each HAA (US EPA, 2003). IC was investigated first as it offered a fast and cheap method, and subsequently three GC methods were evaluated. The GC methods were (1) GC coupled with MS, (2) a two dimensional GC coupled with time of flight mass spectrometry (TOFMS) and (3) GC coupled with ECD. The most suitable method was then validated according to the US EPA methods (1995, 2003).

## 3.2 METHOD COMPARISON FOR HAA ANALYSIS

The purpose of this section was to compare four analytical methods, to determine the most suitable one for the quantification of HAAs.

### 3.2.1 Materials and Methods: IC

#### *3.2.1.1 Reagents and glassware*

Standards were individually available from Sigma-Aldrich Ltd (UK). The standards used were MCAA at 99% purity, MBAA at 99+%, DCAA at 99+%, BCAA at 97%,

TCAA ACS reagent at 99+%, DBAA at 97%, BDCAA, neat, at 99+%, DBCAA, neat, at 99+%, and TBAA at 99%. Reagent water used in the preparation of calibration standards and blanks was prepared using PURELAB Ultra Genetic 18.2 MΩ-cm pure water (ELGA LabWater, UK).

All glassware was meticulously washed with deionised water, soaked in a 5% nitric acid solution for 12 hours, rinsed with deionised water three times and heated in a standard dryer until thoroughly dry. Because the accuracy of conical flasks can be affected by the standard dryer, they were placed on a drying rack until thoroughly dry.

#### *3.2.1.2 Preparation of standards*

The stock standard solutions were prepared in pure water. Stock solution 1 was prepared at a concentration of approximately 10 mg/L for each compound. A secondary standard solution at a concentration of 100 µg/L was prepared for each compound individually. Calibration standard concentrations were 5, 25, 50 and 100 µg/L. The concentrations 5, 25 and 50 µg/L were achieved by mixing and diluting the secondary stock solution. The concentration 100 µg/L was achieved by mixing and diluting the stock solution 1. Calibration standards were made freshly. Stock solutions were kept refrigerated and were discarded after one month.

#### *3.2.1.3 Method description*

Before commencing the analysis, all 5 mL standards/samples were treated with two cartridges. The first contained silver to remove chloride and the second was used to remove any residual dissolved silver (OnGuard II Ag and OnGuard II H, Dionex, UK). This method was first reported by Liu and Mou (2003). No chlorine was added to the standard, but cartridges were used to make sure that the standards were treated the same as the samples.

The analysis was performed at room temperature with all samples injected in duplicate. The following HAAs were determined: MCAA, MBAA, DCAA, BCAA, TCAA, DBAA, BDCAA, DBCAA and TBAA.

#### *3.2.1.4 Instrumentation conditions*

Analysis of the nine HAAs was carried out with an IC system (Dionex, DX500 series, UK). This consisted of an Ion Pac AG9HC guard column (4 x 50 mm), an IonPac AS9HC separation column (4 x 250 mm), an anion electrolytic suppressor (Atlas, 4 mm, UK) in auto-suppression recycle mode, an SC 20 suppressor controller, an electrochemical detector (ED 40) in conductivity mode and a 250 µL sample loop (all supplied by Dionex, UK). The eluent was 11.5 mM sodium carbonate ($Na_2CO_3$) anhydrous with which all the HAAs could be well separated and detected. The suppressor current was set to 85 mA and the eluent flow rate was kept at 1.0 ml/min. This method was first reported by Liu and Mou (2003).

### 3.2.2 Materials and Methods: GC

The GC methods were (1) GC coupled with MS, (2) a two dimensional GC coupled with TOFMS and (3) GC coupled with ECD. The procedure for standard/sample preparation was identical for the three GC methods. The HAAs measured with GC methods were MCAA, MBAA, DCAA, BCAA, TCAA and DBAA and are referred as $HAA_6$. At the time of this study, only these six HAAs were commercially available at the same concentration in a certified mixture.

#### *3.2.2.1 Reagents and glassware*

The solvent use for the extraction work was MtBE, HPLC grade, (Fisher Scientific, UK). The internal standard was 99+% pure 1,2,3-trichloropropane (Fisher Scientific, UK). The acidic methanol solution was prepared with concentrated sulphuric acid ($H_2SO_4$), density of 1.83 g/mL and >95% pure, and reagent grade methanol (Fisher Scientific, UK). Sodium sulphate ($Na_2SO_4$) (Fisher Scientific, UK) was 99% extra pure anhydrous and was baked overnight at 100°C before the extraction. The standards were available as EPA 552 halogenated acetic acids mix in a 1 mL ampoule from Sigma-Aldrich Ltd (UK). Purities for the $HAA_6$ ranged between 97.4 and 99.9% and were supplied at 2000 µg/mL each. Reagent water used in the preparation of calibration

standards and blanks was prepared from PURELAB Ultra Genetic 18.2 MΩ-cm pure water (ELGA LabWater, UK).

All glassware was meticulously washed with deionised water, soaked in a 5% nitric acid solution for 12 hours, rinsed with deionised water three times and heated in a standard dryer until thoroughly dry. Because the accuracy of conical flasks can be affected by the standard dryer, they were placed on a drying rack until thoroughly dry.

#### *3.2.2.2 Preparation of standards*

Stock solution 1 was prepared in MtBE at a concentration of approximately 20 mg/L for each compound by accurately transferring 50 µL of the EPA halogenated acetic acids mix to a 5 mL volumetric flask. Calibration standard solutions were prepared by diluting stock 1 in 100 mL volumetric flask with pure water. Stock 1 and calibration standards were prepared freshly and discarded after use.

#### *3.2.2.3 Method description*

HAAs are highly water-soluble DBPs that exist as ions at ambient pH. They must be converted to their volatile methyl ester form to be analysed with GC (Singer et al., 2002). The derivatisation method used here was reported by Tung et al. (2006) and is a modified version of US EPA Method 552.2 (1995) (Figure 3.1).

A 30 mL volume of sample was adjusted to a pH of 0.5 or less and extracted with 3 mL of MtBE containing an internal standard. The protonated HAAs that have been partitioned into the organic phase were then converted to their methyl esters by the addition of acidic methanol followed by heating at 50ºC for 2 hours. The solvent phase containing the methylated HAAs was separated from the acidic methanol by addition of 4 mL of a 10% aqueous solution of sodium sulphate. The aqueous phase was discarded. The solvent phase was removed for analysis with (1) GC/MS, (2) GCxGC/TOFMS and (3) GC/ECD.

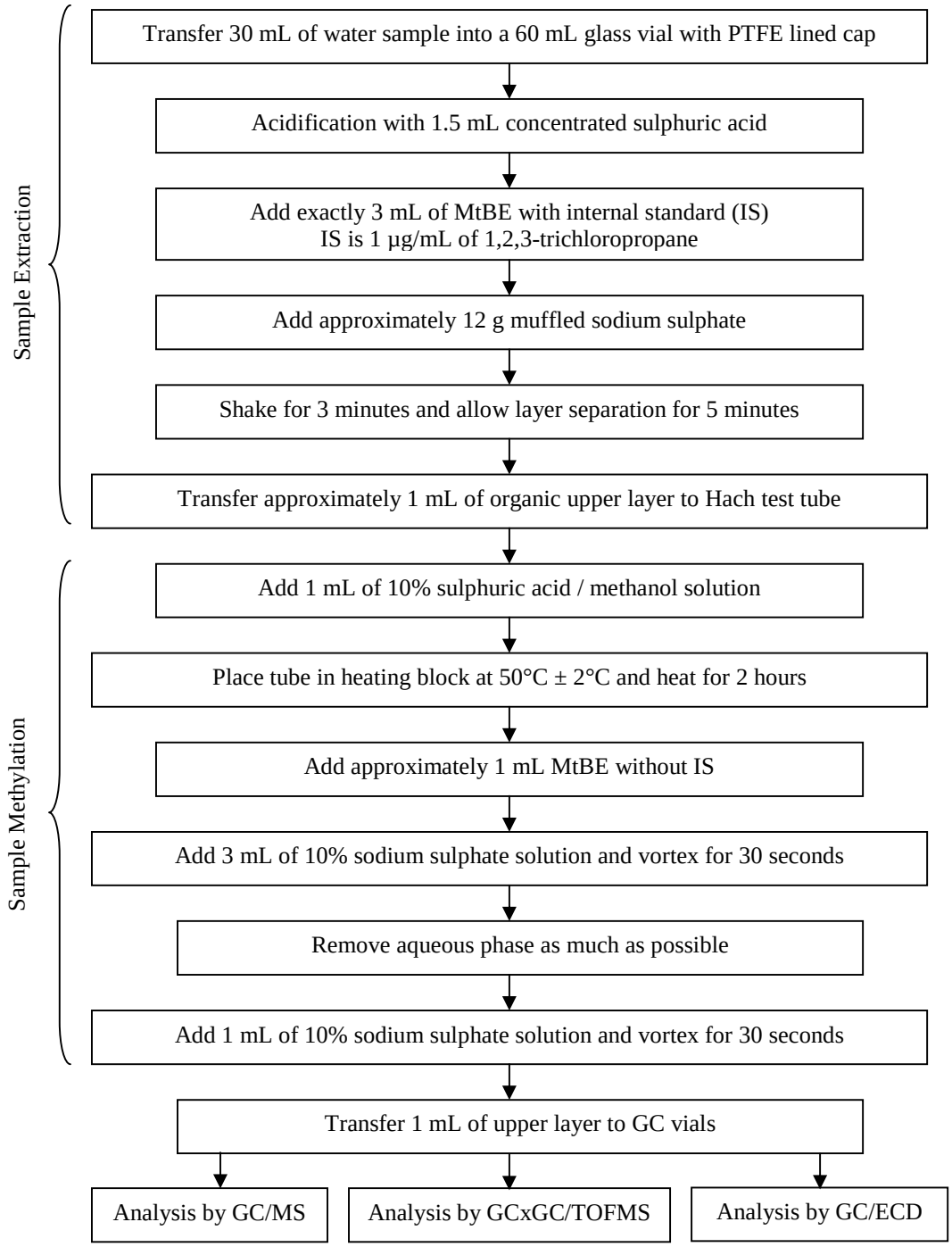



Figure 3.1 Sample preparation procedure (Tung et al., 2006) – Adapted from US EPA Method 552.2 (1995)

*Optimisation of the US EPA Method 552.2 (1995)*

Under the US EPA Method 552.2 methylation conditions, a complete methylation was observed for MXAAs and DXAAs, but not for the four TCAAs (Xie et al., 2002). It was concluded by the same study that improvement of methylation efficiency could be

achieved by working with an MtBE:acidic methanol ratio of 1:1, which is applied here. Also, in the revised method, sodium sulphate solution ($Na_2SO_4$) was used to replace sodium bicarbonate ($NaHCO_3$) recommended in the US EPA Method 552.2 (1995). Indeed it was reported that the release of carbon dioxide ($CO_2$) from sodium bicarbonate may result in a loss of HAA methyl esters (La Guardia, 1996).

#### *3.2.2.4 Instrumentation conditions*

*GC/MS*

HAA standards were run on a GC Perkin Elmer AutoSystem XL coupled with a TurboMass Gold MS using the method reported by Xie (2001). This method involved a gas flow rate of 1.0 mL/min. The oven temperature was set at 35°C and raised gradually to 185°C. The injector temperature was 200°C, the ion source temperature was 230°C and the electron energy was 70 eV.

To confirm the results found here, samples were also run on a GC Agilent 5973 interfaced with quadrupole MS. An injection volume of 1 µl of the HAA calibration standard was introduced splitless into a BPX 5 GC column (SGE, UK; 30 m × 0.25 mm × 0.25 µm). The initial GC oven temperature was set at 55ºC and held for 2 minutes. The temperature was then raised at a rate of 5ºC/min to 220 ºC. The GC injector temperature was maintained isothermally at 200ºC. A constant flow rate of 99.999 % pure inert helium gas was held at 1 ml/min. The MS parameters used were: transfer line temperature 280ºC, manifold temperature and source temperature 230ºC, and the electron energy was 70 eV.

Total ion chromatograms were obtained (m/z 35 – 300) and the following two ions, m/z 59 and 75 were selected for analysis. The m/z 59 ion is the base peak for the HAA methyl esters and m/z 75 is the base peak for the IS. The MassTransit software was used for data conversion and an Agilent ChemStation G1701DA was used for data handling and processing.

*GCxGC/TOFMS*

HAA samples were run in parallel by comprehensive two dimensional GC/MS utilising a Leco Pegasus VI GC×GC/TOFMS (Figure 3.2). GC×GC separation was performed using an Agilent 6890 GC with a Leco GC×GC modulator fitted coupled to a Pegasus IV TOFMS (LECO Corporation, Michigan, US).

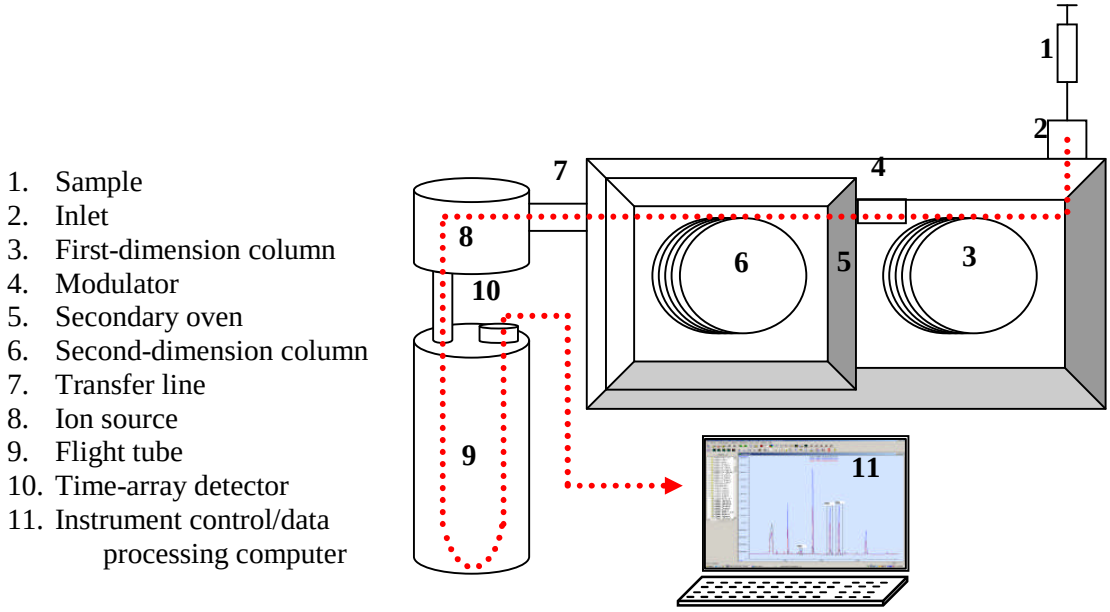



Figure 3.2 Simplified diagram of GCxGC/TOFMS Instrument

The GC injector was operated in splitless mode with a column flow rate of 1.0 mL/min and held at 200°C. GC×GC separation utilised a non-polar column and a polar column: a BPX5 (SGE, UK; 30 m × 0.25 mm × 0.25 μm) and a BPX50 (SGE, UK; 1.8 m × 0.1 mm × 0.1 μm) respectively. The GC oven temperature was held for 1 minute at 35°C and ramped to 220°C at a rate of 5°C/min and then held for 1 minute, the second column was ramped at 30°C above the first column. Modulation time was 4 seconds. Mass spectra were acquired in electron ionisation mode from 33 to 400 amu with an acquisition rate of 133 spectra per second.

*GC/ECD*

HAAs were also measured on a GC with an ECD (Agilent 6890). A volume of 1 µL was injected with the injector set at 200°C with a 5:1 split ratio. The separation was performed using a BPX5 column (SGE, UK; 30 m × 0.25 mm × 0.25 µm) with a helium carrier gas at a column flow rate of 1.1 ml/min. The initial oven temperature was 35°C followed by a 5°C per minute temperature ramp to 220°C and held for 1 minute. The detector temperature was 230°C and the rate of data collection 20 Hz.

### 3.2.3 Results and Discussion

#### *3.2.3.1 IC method*

HAA standards were first run individually with IC to determine their retention time. A typical IC chromatogram for a 10 µg/L mixture of $HAA_9$ is shown (Figure 3.3). As shown in Table 3.1, all the coefficients of determination of linear regression were above 0.9644, which expressed a linear calibration curve for each of the nine HAAs. This compares well with Liu and Mou (2003) (Table 3.1).

Table 3.1 Calibration correlation coefficients for $HAA_9$ analysed by IC in this present study and in a study by Liu and Mou (2003)

| HAA | Correlation coefficients ($R^2$) | |
|---|---|---|
| | Present study | Liu and Mou (2003) |
| MCAA | 0.9997 | 0.9992 |
| MBAA | 0.9985 | 0.9988 |
| DCAA | 0.9991 | 0.9990 |
| BCAA | 0.9997 | 0.9989 |
| DBAA | 0.9943 | 0.9886 |
| TCAA | 0.9916 | 0.9993 |
| BDCAA | 0.9888 | 0.9991 |
| DBCAA | 0.9890 | 0.9884 |
| TBAA | 0.9644 | 0.9889 |

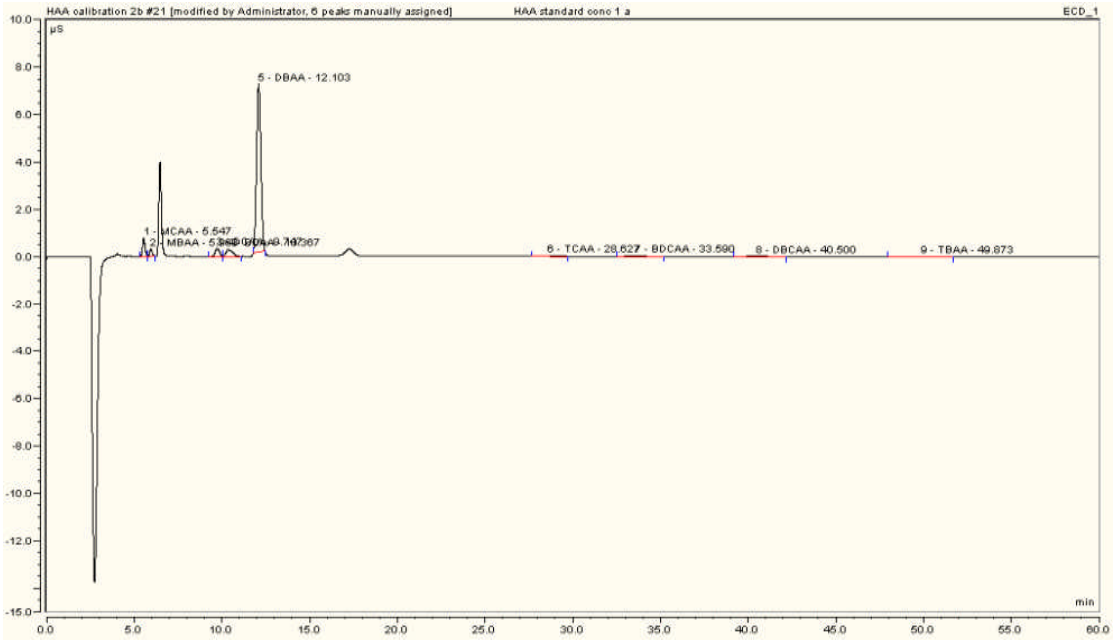



Figure 3.3 Chromatogram of $HAA_9$ standards (10 µg/L each). Retention time (minutes): MCAA = 5.547, MBAA = 5.960, DCAA = 9.767, BCAA = 11.367, DBAA = 12.103, TCAA = 28.627, BDCAA = 33.590, DBCAA = 40.500, TBAA = 49.873

Limits of detection (LOD) were calculated as three times the signal-to-noise ratio for $HAA_6$ (MCAA, MBAA, DCAA, BCAA, TCAA, DBAA) and $HAA_3$ (BDCAA, DBCAA and TBAA) and were defined as the smallest concentration that can be determined which can be expected to be distinguishable from the blank measurement (Quevauviller, 2002). LOD was determined by spiking calibration standards into upland, ground and lowland water. The detection limits of the analytes achieved with the column and the suppressor ranged between 2.6 and 16.5 µg/L for $HAA_6$ and between 11.7 and 31.9 µg/L for $HAA_3$ (Table 3.2). Liu and Mou (2003) reported greater LOD for $HAA_6$ between 0.37 and 2.16 µg/L and comparable LOD for $HAA_3$ between 8.17 and 31.64 µg/L in deionised water. Nair et al. (1994) found LOD for five HAAs (MCAA, MBAA, DCAA, TCAA and DBAA) above 8.0 µg/L, which is higher than the values reported here. The limits of detection observed here for $HAA_6$ are higher than those reported by Liu and Mou (2003) and were believed to be a result of the matrix impact. The criterion to accept a method here was LOD of 0.17 µg/L for a single HAA; hence, LOD for $HAA_3$ was poor as none of them could be detected below 10 µg/L.

Table 3.2 Detection limits for the analytes from this present study, Liu and Mou (2003) and Nair et al. (1994)

| Waters | $HAA_6$ (µg/L) | $HAA_3$ (µg/L) |
|---|---|---|
| Ground water | 5.0 – 16.5 | 21.4 – 26.8 |
| Upland water | 2.6 – 11.0 | 13.8 – 23.0 |
| Lowland water | 3.2 – 14.1 | 11.7 – 31.9 |
| Deionised water (Liu and Mou, 2003) | 0.4 – 2.2 | 8.2 – 31.6 |
| Deionised water (Nair et al., 1994) | 8.0 – 80.0[a] | NR[b] |

[a] Data available for 5 HAAs (MCAA, MBAA, DCAA, TCAA and DBAA); [b] Not reported.

The choice of an IonPac AS9HC column is explained by Liu and Mou (2003). They reported that fluoride, naturally present in the water, MCAA, MBAA and chloride are weakly retained anions, and if the retention time of fluoride, MCAA and MBAA are close to that of chloride, the high response of chloride will seriously interfere with the other anions. Hence in order to separate these four anions well, a high capacity column on which the anions could be tightly bound was preferred (i.e. IonPac AS9HC column). With the use of carbonate as eluent, the nine HAAs were well separated. The Atlas anion electrolytic suppressor, used here, exchanged the cations from the eluent (aqueous $Na_2CO_3$) for hydronium ions ($H_3O^+$) forming carbonic acid ($H_2CO_3$) of low conductivity, and exchanged sample for fully protonated HAAs of high conductivity. Hence better detection sensitivity has been observed with suppressed IC than with non-suppressed IC (Jauhiainen et al., 1999).

The advantage of the IC was the simplicity and the speed of sample preparation (about 10 minutes), but GC methods were reported to be more sensitive and were believed to be more suitable for the measurement of HAAs in UK treated water. Hence no further work was undertaken with IC.

#### *3.2.3.2 GC methods*

GC/MS was used to analyse six HAA standards that had been derived to their methyl esters. The GC/MS method was reported by Xie (2001), and although he was able to resolve all the nine HAAs with GC/MS (Figure 3.4 A), the peaks, in this present study, were not well resolved nor was the signal-to-noise ratio sufficient. The GC/MS was run

in the selective ion monitoring (m/z = 59) mode but this did little to improve the resolution and the sensitivity. It was not possible to determine limits of detection for this method. In order to confirm the findings, samples were run in parallel using another GC/MS (Agilent 5973) (Figure 3.4 B). The results were comparable to the GC/MS Perkin Elmer Turbomass.

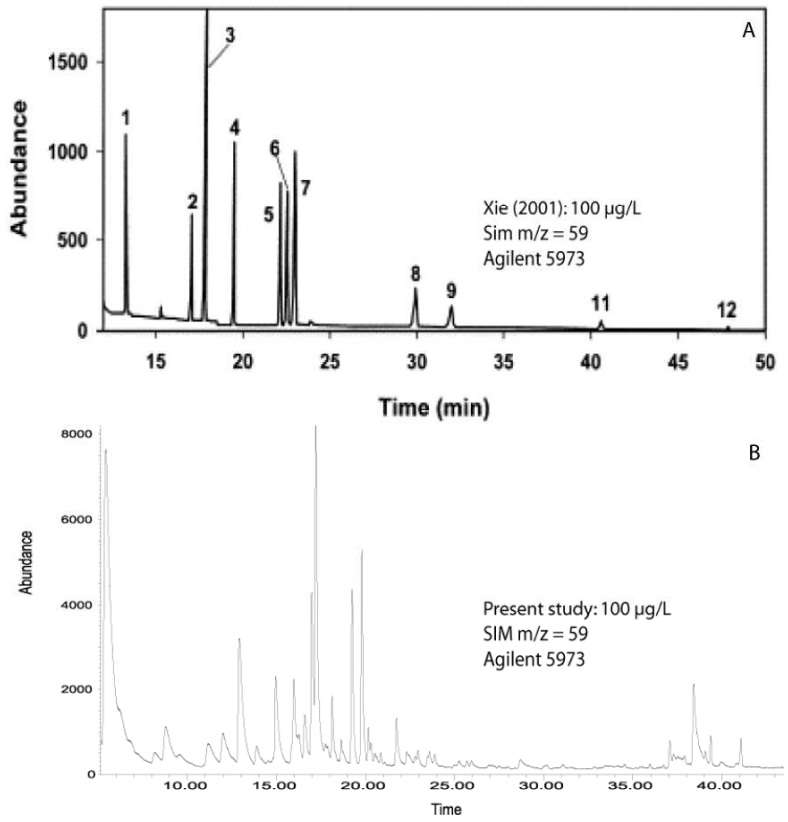
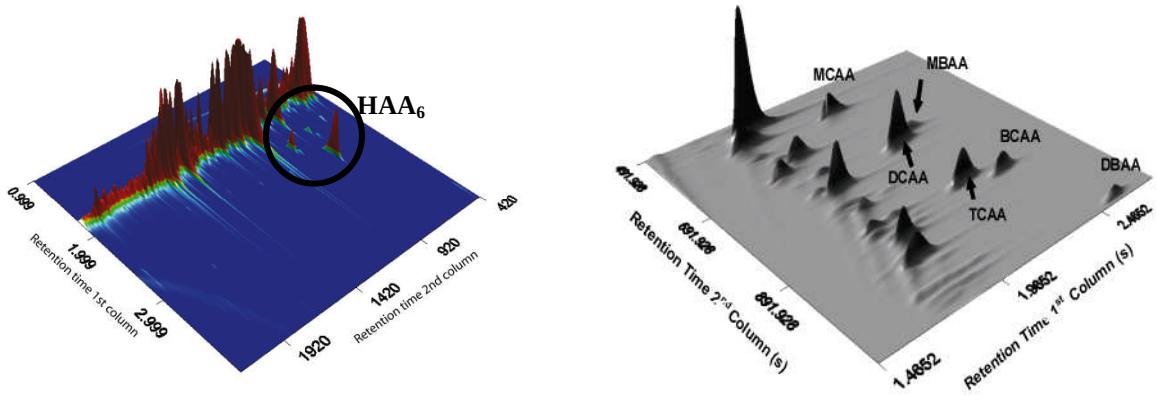



Figure 3.4 Comparison of a 100 µg/L of each derived HAA standard chromatograms from two similar GC/MS instruments by (A) Xie (2001) and (B) this present study

To investigate the lack of resolution and sensitivity further, samples were run using a Leco Pegasus 4D GC×GC/TOFMS. This machine uses two GC columns to separate analytes based on volatility as well as polarity. The derived HAA methyl ester peaks could be observed as they had been separated from the interfering material (Figure 3.5 A+B), but the interfering material had a greater intensity than some of the derived methyl esters and also eluted at retention times that overlapped with the derived HAA methyl esters (Figure 3.5 A). The interfering peaks are thought to be incurred from the derivatisation procedure, but to date, have not been identified.




**A** **B**

Figure 3.5 (A) Total ion chromatogram for derived $HAA_6$ (equivalent to 100 µg/l of each HAA) and (B) a partially reconstructed mass chromatogram (m/z = 59) of a derived $HAA_6$ standard at 100 µg/l of each HAA (Leco Pegasus 4D GC×GC/TOFMS)

Despite the effectiveness and the enhanced separation of the GCxGC/TOFMS, no further work was undertaken with this instrument due to availability and the cost of analysis.

HAA analysis was then considered with GC/ECD. A derived $HAA_6$ standard at 100 µg/L of each HAA was run with a GC/ECD (Agilent 6890). The six HAAs gave good responses and no interfering peaks were observed (Figure 3.6). The advantage of the ECD is the selectivity and approved methods reported LOD for HAAs in the low µg/L range (US EPA, 1995, 2003). Indeed, the ECD is particularly sensitive to halogens because the detection is based on how much the halogens capture electrons produced by a Beta particle (electron) emitter (Lovelock, 1958; Lovelock, 1974). The GC/ECD method, however, requires labour-intensive and fastidious extraction (6 hours). Nevertheless it was found to be the most appropriate analytical device for the analysis of HAAs in UK treated water and the validation work is presented in Section 3.3.

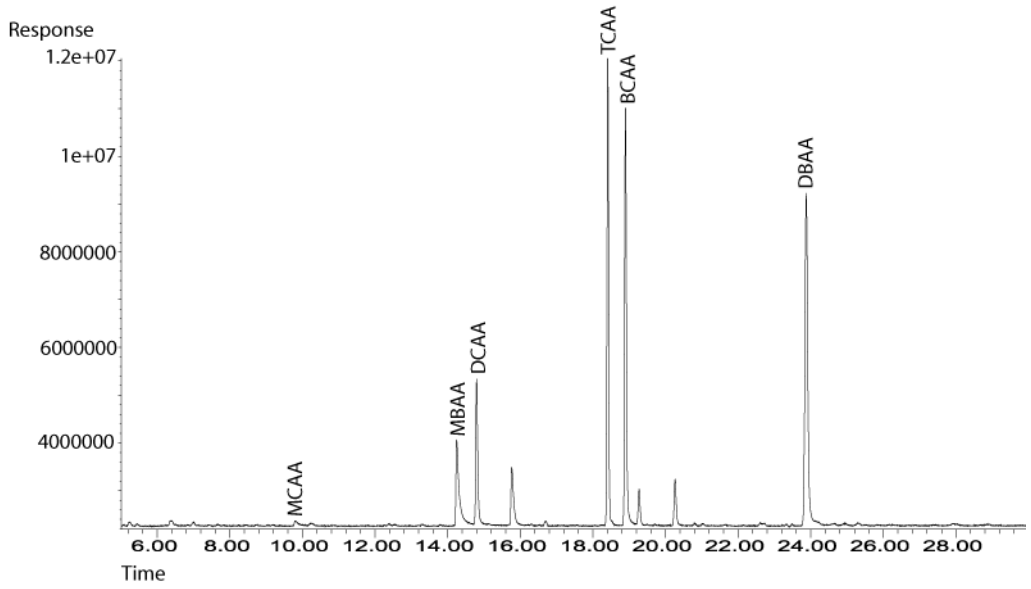



Figure 3.6 Chromatogram for a diluted (equivalent to 100 µg/l of each) and derivatised $HAA_6$ standard with GC/ECD

### 3.2.4 Conclusion

Here four different methods were investigated for the determination of HAAs. With IC, the detection limits for $HAA_6$ were between 2.6 and 16.5 µg/L and between 11.7 and 31.9 µg/L for $HAA_3$. LOD for $HAA_9$ were well above the level required to accept the method and IC was not deemed sensitive enough for the work here. Due to interfering peaks overlapping HAAs, GC/MS was not suitable for the measurement of HAAs. GCxGC/TOFMS is a very selective and effective tool, but expensive. Despite its labour-intensive requirements, GC/ECD was selected as the best suitable analytical device for the quantification of HAAs for the remaining work in this thesis.

## 3.3 GC/ECD METHOD VALIDATION

The validation of nine HAAs was determined in compliance with the US EPA Method 552.2 (1995) and 552.3 (2003). The nine HAAs are referred as $HAA_9$.

### 3.3.1 Materials and Methods

#### *3.3.1.1 Reagents and glassware*

The reagents were identical to those in Section 3.2.2.1, except for the EPA 552.2 haloacetic acids mix in a 1 mL ampoule from Sigma-Aldrich Ltd (UK). Purities for the $HAA_9$ ranged between 96.2 and 99.9% and were concentrated at 2000 µg/mL each. All glassware was treated as in Section 3.2.2.1. Ammonium chloride ($NH_4Cl$) (Fisher Scientific, UK) at a concentration of 100 mg/L was used as a quench agent and has been shown to not degrade any HAAs, and especially $HAA_3$ (BDCAA, DBCAA and TBAA) (Singer et al., 2002).

#### *3.3.1.2 Preparation of standards*

Standard preparation was explained in Section 3.2.2.2.

#### *3.3.1.3 Method description*

The method was explained in Section 3.2.2.3 (Figure 3.1). Here the solvent phase was removed for analysis with GC/ECD only.

#### *3.3.1.4 Instrumentation conditions*

HAA standards and samples were run with a different Agilent 6890 GC/ECD than the one used in Section 3.2.2.4. A volume of 1 µL was injected with the injector set at 200°C with a 10:1 split ratio. Separation was performed by a ZB-1ms column (Phenomenex, UK; 30 m × 0.25 mm × 0.25 µm) with a helium carrier gas at a column flow rate of 0.9 mL/min. The initial oven temperature was 35°C and held for 8 minutes followed by an 8°C per minute temperature ramp to 200°C and held for 1 minute. The total run time was 29.63 minutes. The detector temperature was 270°C and the rate of collection data was 20 Hz.

*3.3.1.5 Method performance*

The average retention time for each HAA was determined with seven replicates of a derived 1.0 µg/L of each HAA and internal standard aqueous standard. The retention time precision was evaluated by calculating the relative standard deviation (RSD) as recommended by US EPA Method 552.3 (2003). The RSD of the sample replicate analyses must be less than 20% and was calculated with the following equation:

$$\text{RSD (\%)} = \left(\frac{\text{Standard deviation of array X}}{\text{Mean of array X}}\right) \times 100 . \qquad \text{Equation 3.1}$$

Seven replicates of a derived 0.10 µg/L and 1.00 µg/L of each HAA aqueous standard were extracted and analysed over a period of three days for determining LODs. Ammonium chloride, which was the HAA preservative agent, was added to the standards at the same concentration as that used to quench the samples. LOD was calculated using the following equation:

$$\text{LOD} = \text{St}_{(n-1,\, 1-\alpha\, = 0.99)} \qquad \text{Equation 3.2}$$

where: $t_{(n-1,\, 1-\alpha\, = 0.99)}$ = Students t value for the 99% confidence level with n-1 degrees of freedom,

n = number of replicates, and

S = standard deviation of the replicate analyses.

Blanks were not subtracted when performing LOD calculations.

The analyte recovery was determined by analysing two treated water samples spiked with three levels of HAAs. Fortifications were at 5, 25 and 75 µg/L. The recovery for each analyte was calculated using the following equation:

$$\text{R} = \frac{(\text{D} - \text{E})}{\text{F}} \times 100\% \qquad \text{Equation 3.3}$$

where: D = measured concentration in the fortified sample,

E = measured concentration in the unfortified sample, and

F = fortified concentration.

#### *3.3.1.6 Water samples*

Treated water samples used to determine the analyte recovery were geographically different. The lowland and the upland waters were collected from South East England and northern England respectively. The treatment of the lowland water consisted of ozonation, coagulation, GAC and chlorination, whereas the treatment of the upland water was coagulation, sand filtration and chlorination. Both treated samples were collected prior to chlorination at the water treatment works.

### 3.3.2 Results and Discussion: Evaluation of method performance

HAA analysis with GC/ECD is widely used and ECD has been proven to be very selective and sensitive to HAAs. However quality controls were required prior to analyte quantification. Chromatograms for nine HAAs and internal standard were obtained by running a standard using the chromatographic conditions described in Section 3.3.1.4. The retention times for all nine HAAs and internal standard are listed in Table 3.3. The RSD calculated for the retention times reported here were typically low and were similar to those reported by US EPA Method 552.3 (2003), demonstrating good reproducibility of the method.

Table 3.3 Identification of the compounds and method performance

| Peak no. | Compound | Average tr[a] (min) | RSD[b] (%) | $R^2$ | Fortification level (µg/L) | Detection Limit[c] (µg/L) | MRL[d] (µg/L) |
|---|---|---|---|---|---|---|---|
| 1 | MCAA | 6.69 | 0.104 | 0.999 | 1.00 | 0.783 | 2.349 |
| 2 | MBAA | 9.86 | 0.030 | 0.999 | 0.10 | 0.086 | 0.258 |
| 3 | DCAA | 10.42 | 0.019 | 0.996 | 1.00 | 0.317 | 0.951 |
| 4 | BCAA | 13.21 | 0.012 | 0.999 | 0.10 | 0.026 | 0.078 |
| 5 | TCAA | 13.37 | 0.011 | 0.996 | 1.00 | 0.064 | 0.192 |
| 6 | DBAA | 15.37 | 0.006 | 0.998 | 0.10 | 0.022 | 0.066 |
| 7 | BDCAA | 15.76 | 0.009 | 0.994 | 0.10 | 0.037 | 0.111 |
| 8 | DBCAA | 17.80 | 0.010 | 0.991 | 0.10 | 0.055 | 0.165 |
| 9 | TBAA | 19.83 | 0.067 | 0.987 | 0.10 | 0.045 | 0.135 |
| IS | IS[e] | 12.97 | 0.010 | NA[f] | NA[f] | NA[f] | NA[f] |

[a] The average retention time corresponds to the average of seven injections; [b] Corresponds to the relative standard deviation and must be less than 20% according to US EPA Method 552.3 (2003); [c] Fortified waters were extracted and analysed over 3 days for seven replicates; [d] Corresponds to the minimum reporting level and is the threshold expected for accurate quantification in an unknown sample. It has to be at least three times the limit of detection; [e] 1,2,3-trichloropropane; [f] Not applicable.

A typical GC/ECD chromatogram for a 100 µg/L of $HAA_9$ derived standard is shown (Figure 3.7) and peaks were identified in Table 3.3. The highest peak was DBAA followed by BDCAA, TCAA and other HAAs. Similar responses were published in the US EPA Method 552.3 (2003). The response is proportional to the electrons attracted toward the halogen, which induces a reduction of the current generated by the ECD. Although the electronegativity of chlorine is greater than that of bromine (3.16 and 2.96 Pauling respectively), MBAA captured more electrons than MCAA. This is believed to be related to the intermolecular forces present in the methyl ester form of the HAAs. MCAA had the smallest ECD response and this is supported by the US EPA Methods 552.2 (1995) and 552.3 (2003). The chromatograms presented in the US EPA Method 552.3 (2003) reported different orders of elution for BCAA, TCAA, DBAA, BDCAA and internal standard compared to the method reported here. The main reason is explained by the polarity of the column used for analysis. Here the column was a ZB-1ms and has a lower polarity than the columns DB-1701 and DB-5.625 used in the US EPA Method 552.3 (2003). The time spent by each solute in the stationary phase was therefore variable depending on the column polarity. Therefore the retention factor, which is the ratio of the amount of time a solute spends in the stationary phase and mobile phase, varied for each species between columns. Unknown peaks were observed, but did not interfere with HAAs and internal standard.

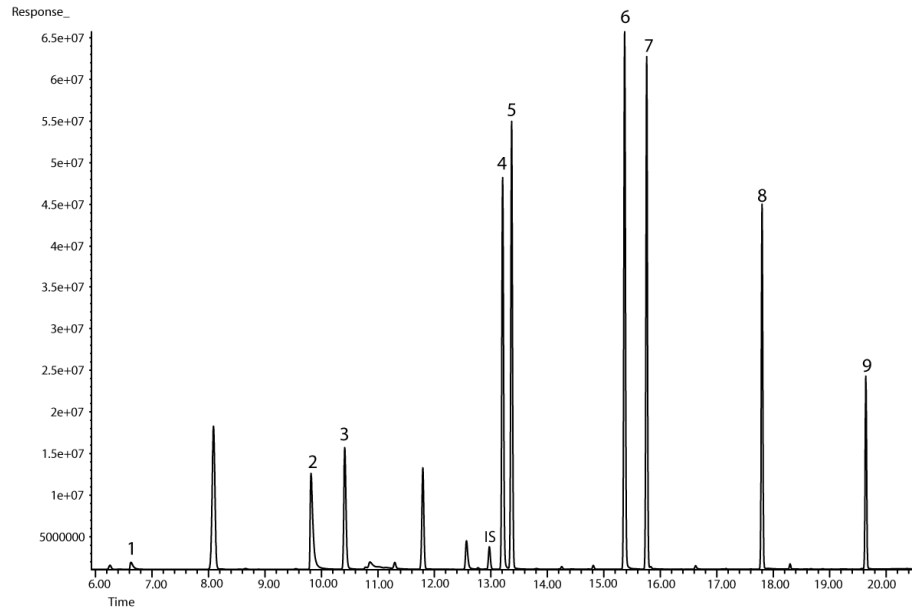



Figure 3.7 GC/ECD chromatogram for a derived $HAA_9$ standard (100 µg/L) (see Table 3.3 for analyte identification)

Calibration was performed by extracted procedural standards, i.e. fortified pure water, by the procedure in Section 3.2.2.3. The US EPA Method 552.2 (1995) recommended, five calibration standards, here six calibration points were plotted and were 0.5, 5, 25, 50, 75 and 100 µg/L. The calibration curves were generated by plotting the area ratios ($A_{HAA}/A_{IS}$) against the concentration $C_{HAA}$ of the six calibration standards (Figure 3.8)

where: $A_{HAA}$ = the peak area of the HAA

$A_{IS}$ = the peak area of the internal standard

$C_{HAA}$ = the concentration of the HAA.

A linear calibration curve was obtained for each of the nine HAAs and no HAA was detected in pure water free of HAA spikes. The coefficients of determination of linear regression are reported in Table 3.3 and were all above 0.987.

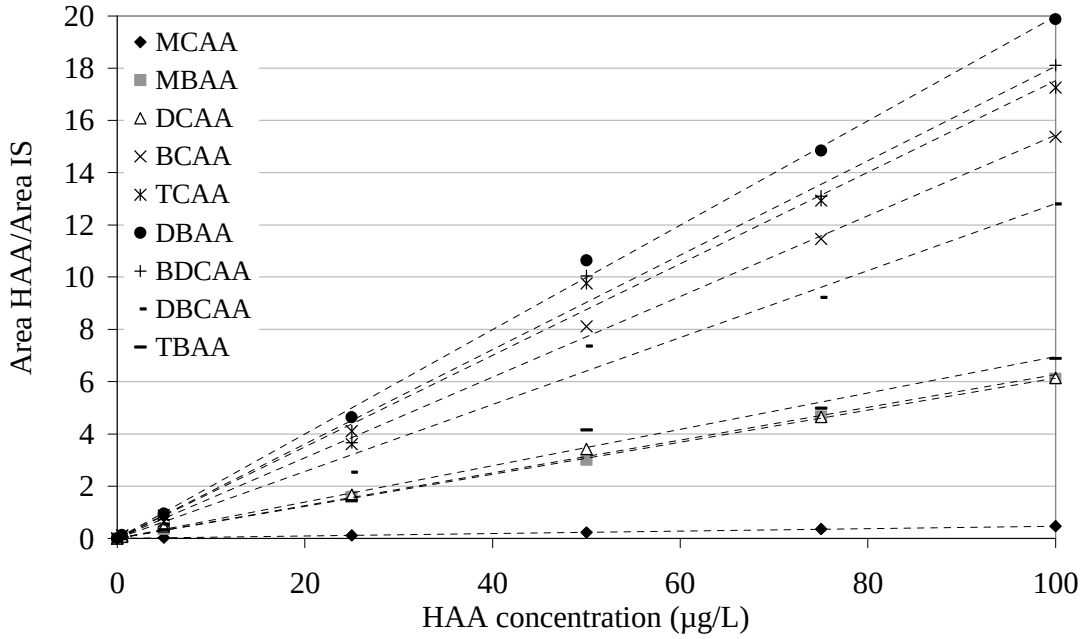



Figure 3.8 Calibration curves for nine HAAs – Concentration: 0.5, 5, 25, 50, 75 and 100 µg/L

The LOD (Table 3.3) for MCAA was 0.783 µg/L, which is higher than the values 0.273 µg/L and 0.17 µg/L reported by the US EPA Method 552.2 (1995) and US EPA Method 552.3 (2003) respectively. The variation of MCAA LOD is caused by the varying GC/ECD sensitivity between studies. LOD for DCAA was 0.317 µg/L and is comparable with the US EPA Method 552.2 (1995), and similar to that reported by Malliarou et al. (2005) who found DCAA LOD at 0.8 µg/L using the US EPA Method 552.2 (1995). LODs for the remaining HAAs were greater than these reported by the US EPA Method 552.2 (1995). The improved LOD is mostly due to the optimisation of the experimental method. The total LOD for the nine HAAs was 1.435 µg/L. For comparison, the LOD standards were sent to a collaborative laboratory (Open University, Milton Keynes, UK), where they found a LOD of 1.494 µg/L for the nine HAAs, which is very comparable. Malliarou et al. (2005) reported an LOD for 6 HAAs (MBAA, DCAA, BCAA, TCAA, DBAA and BDCAA) of 4.9 µg/L. In relation to LOD, the minimum reporting level (MRL) for each HAA was calculated (Table 3.3). The MRL, which is at least three times the LOD, corresponds to the threshold expected for accurate quantification in an unknown sample. Except for MCAA, the remaining HAAs

could be well quantified below 1 µg/l. It was decided to accept MRL below 0.5 µg/L (e.g. BCAA at 0.078 µg/L) considering that the interpolation of the calibration curves were good and there is a high likelihood that concentrations below the lowest calibration standards are accurately quantified.

Analyte recoveries exhibited bias in both water samples (Table 3.4). The guideline provided by the US EPA Method 552.3 (2003) recommends that recoveries should range between 70 and 130%, except for the low level of fortification, where 50 to 150% is acceptable. BCAA and DBAA were found to be biased in both waters. This is mostly caused by matrix interferences, such as contaminants that are co-extracted from the sample (US EPA, 2003). DCAA was also found to be biased in the upland water. This may be due to the significant background of DCAA present in the unfortified matrix (US EPA, 2003). The remaining HAAs were well recovered and RSD were acceptable for all HAAs at all levels. Because some recoveries of DCAA, BCAA and DBAA fell outside the designated range, concentrations of these analytes in real water would have to be corrected to obtain meaningful values.

Table 3.4 Spike recovery in lowland and upland water fortified with HAAs

| LOWLAND WATER SAMPLE | | | | | | |
|---|---|---|---|---|---|---|
| Compounds | Fortification at 5 µg/L | | Fortification at 25 µg/L | | Fortification at 75 µg/L | |
| | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) |
| MCAA | 132 | 9.3 | 120 | 12.0 | 112 | 1.1 |
| MBAA | 121 | 5.5 | 106 | 5.1 | 102 | 1.5 |
| DCAA | 150 | 2.8 | 130 | 1.1 | 123 | 1.4 |
| BCAA | 143 | 1.9 | **138**[b] | 1.3 | **136**[b] | 1.8 |
| TCAA | 111 | 5.2 | 113 | 5.7 | 115 | 6.1 |
| DBAA | 143 | 3.0 | **150**[b] | 2.1 | **148**[b] | 2.9 |
| BDCAA | 90 | 7.9 | 103 | 9.3 | 111 | 8.7 |
| DBCAA | 84 | 11.0 | 90 | 11.2 | 98 | 11.5 |
| TBAA | 76 | 16.4 | 71 | 13.1 | 77 | 14.1 |
| UPLAND WATER SAMPLE | | | | | | |
| Compounds | Fortification at 5 µg/L | | Fortification at 25 µg/L | | Fortification at 75 µg/L | |
| | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) |
| MCAA | 122 | 3.6 | 119 | 5.2 | 117 | 1.9 |
| MBAA | 132 | 3.5 | 117 | 2.2 | 109 | 1.1 |
| DCAA | **153**[b] | 3.7 | **131**[b] | 1.1 | 121 | 1.4 |
| BCAA | 145 | 1.4 | **136**[b] | 1.1 | **133**[b] | 1.1 |
| TCAA | 119 | 3.2 | 115 | 3.1 | 117 | 2.1 |
| DBAA | 146 | 2.3 | **142**[b] | 1.5 | **141**[b] | 1.5 |
| BDCAA | 100 | 6.0 | 103 | 5.1 | 114 | 4.8 |
| DBCAA | 96 | 7.4 | 93 | 6.7 | 103 | 6.5 |
| TBAA | 88 | 10.3 | 81 | 8.5 | 86 | 9.6 |

[a] Corresponds to the relative standard deviation and must be less than 20% according to US EPA Method 552.3 (2003); [b] Corresponds to biased values.

### 3.3.3 Conclusion

The US EPA Method 552.2 (1995), adapted by Tung et al. (2006) was validated here for the quantification of nine HAAs. The method was found to be reproducible and precise with some bias. Linear calibration curves were reported for each HAA. MCAA LOD was high, and this was a result of the GC/ECD sensitivity. The LODs for the remaining HAAs were comparable or greater than the guidelines and the total LOD for the nine HAAs was 1.435 µg/L. Spike recovery calculations showed biased analytes. DCAA, BCAA and DBAA recoveries were believed to be biased due to the matrix effect and concentrations of these found in real samples should be corrected to give realistic values.

## 3.4 CHAPTER SUMMARY

The results presented here showed that GC/ECD was the most suitable analytical device for the measurement of nine HAAs during this thesis (Table 3.5).

Table 3.5 Summary of analytical method conditions and methods performance

| Measuring device | Sample preparation | Analysis time | LOD (µg/L) | References | Suitable for present study |
|---|---|---|---|---|---|
| IC | *Minimal preparation* Cartridges to remove chlorine and silver ~ 10 minutes | < 55 mins | 2.6 – 31.9 | Present study | No |
| | | | 0.4 – 31.6 | Liu and Mou (2003) | |
| GC/MS | *Extensive preparation* Derivatisation (extraction + methylation) US EPA methods ~ 6 hours | < 50 mins | 0.04 – 0.83 | Xie (2001) | No |
| GCxGC/ TOFMS | | NR[a] | NR[a] | Present study | No |
| GC/ECD | | < 30 mins | 0.022 – 0.783 | Present study | Yes |
| | | | 0.820 – 0.066 | US EPA Method 552.2 (1995) | |
| | | | 0.012 – 0.170 | US EPA Method 552.3 (2003) | |

[a] Not reported.

Considering the good calibration curves, it was accepted MRL below 0.5 µg/L and therefore, LOD below 0.17 µg/L for each HAA. The US EPA Method 522.2 (1995), adapted by Tung et al. (2006), was validated according to US EPA Methods 552.2 (1995) and 552.3 (2003). Investigation of the reproducibility, precision and bias demonstrated the reliability of the method.

# Chapter 4

# ANALYTICAL METHODOLOGY FOR SEMI-VOLATILE DBPs

## 4.1 INTRODUCTION

Disinfected water has been shown to contain HAAs and THMs, but there is evidence to suggest that significantly more than 600 chemical DBPs may also exist (Richardson, 1998). There is considerable uncertainty over the identity and levels of DBPs that people are exposed to from drinking water. While most studies have focused on THMs and HAAs, there is a need for comprehensive quantitative occurrence and toxicity data to determine whether other DBPs pose an adverse health risk (Richardson et al., 2003). To address this issue, US nationwide DBP occurrence studies have been undertaken (McGuire et al., 2002; Weinberg et al., 2002). Approximately 50 DBPs, identified in US waters, were rated high priority, because they showed an elevated level of cyto- and genotoxicity (Krasner et al., 2001; Plewa et al., 2004). These DBPs include iodinated-THMs, HANs, HAs, HKs and HNMs and are also referred to as semi-volatile DBPs, due to their Henry's law constant (Krasner et al., 2001). Because they have been discovered more recently than THMs and HAAs and some of these semi-volatile DBPs, such as the HANs, are unstable in aqueous solution (Peters et al., 1990), there has been no regulation promulgated. Nevertheless the WHO has recommended guidelines for two HANs (DCAN at 20 µg/L and DBAN at 70 µg/L) and for one HA (TCA at 10 µg/L) (WHO, 2006). US studies reported levels of DCAN and DBAN below the WHO recommendations (5 and 4 µg/L respectively), whereas TCA reached a maximum of 16 µg/L, which is beyond the WHO guidance (Krasner et al., 2001; Weinberg et al., 2002). An occurrence survey in Canada detected TCA at a level up to 22.5 µg/L, which again exceeds the WHO guidance (Williams et al., 1997). Peters et al. (1990) found levels of less than 1 µg/L for DCAN and DBAN, which are below the US surveys and the WHO recommendations. The other semi-volatile DBPs, such as the i-THMs, HNMs or HKs, have also been detected in treated water at levels up to 19, 10 and 9 µg/L respectively

(Krasner et al., 2006). All these semi-volatile DBPs of health and regulatory concern are being identified in disinfected treated water from all chemical disinfection processes (Krasner et al., 2006) and are therefore believed to be present in UK treated water. To the knowledge of the author, no study has been published reporting levels of i-THMs, HANs, HAs, HKs and HNMs in UK treated water.

In order to determine and to quantify these semi-volatile DBPs, reliable and reproducible methods are necessary. Currently, there is one GC/ECD US EPA approved method: the US EPA Method 551.1 (1995a). This method enables the measurement of 8 semi-volatile DBPs (DCAN, TCAN, BCAN, DBAN, TCA, TCNM, 1,1-DCP and 1,1,1-TCP), four THMs (TCM, BDCM, DBCM and TBM), 8 chlorinated solvents and 17 pesticides/herbicides. In this method, DBPs are extracted from water samples using MtBE and analysed using GC/ECD. The advantages of this method are the short time required for sample preparation (10 minutes) and the short run time to process the 4 THMs and the 8 semi-volatile DBPs (less than 30 minutes). On the other hand, the number of semi-volatile compounds analysed with the US EPA Method 551.1 is limited. Studies on emerging semi-volatile DBPs have focused on synthesised standards that were not previously commercially available and developed new methods that incorporate approximately 50 compounds (Gonzalez et al., 2000; Krasner et al., 2001; Weinberg et al., 2002). These methods assessed, include modified versions of the LLE – GC/ECD US EPA Method 551.1 (1995a) and a SPE – GC/MS to have MS confirmation of the semi-volatile DBPs (Krasner et al., 2001). Quality control demonstrated good reliability of these methods, but SPE methods are more expensive and take more time than LLE. More recently a study by Chinn et al. (2007) reported an automated SPE method combined with GC/ECD and GC/MS for the analysis of 35 DBPs instead of LLE, but reported LLE as having better extraction recoveries compared to SPE.

An insight into the semi-volatile DBP levels in UK treated water was of interest and hence a reliable method for their quantification was required. After comparison of levels of semi-volatile DBPs found in a previous study by Weinberg et al. (2002), 16 DBPs were targeted. The targeted compounds encompassed 12 semi-volatile DBPs: two i-THMs, four HANs, two HAs, two HKs and two HNMs. In addition the four regulated THMs were added to the method. Compared to the US EPA Method 551.1 (1995a), the additional compounds were DCA, DBNM, DCIM and BCIM. By comparison with the

surveys from the Canada, Netherlands and US, previously cited (Peters et al., 1990; Williams et al., 1997; Krasner et al., 2001; Weinberg et al., 2002), it is believed that the analytical method here has to be reliable for low range of µg/L concentrations. Therefore, criteria set for the method are based on accuracy, precision, working range/linearity, selectivity and limit of detection (Fischbacher, 2000). To determine if the method was suitable for the work undertaken here, the MRL chosen was 0.5 µg/L (the lowest standard), which induced a LOD of 0.17 µg/L (Krasner et al., 2001).

The objectives of this chapter were (1) to identify qualitatively the presence of semi-volatile DBPs in UK treated water using SPE – GC/ECD, and (2) to develop a LLE – GC/ECD analytical method for the quantification of the targeted compounds. The primary objective of this chapter was undertaken under the supervision of Dr. Howard Weinberg at the Environmental Sciences and Engineering department laboratory of University of North Carolina (UNC, Chapel Hill, US). Work continued in the UK at Cranfield University to complete the secondary objective of this chapter.

## 4.2 QUALITATIVE IDENTIFICATION OF THE SEMI-VOLATILE DBPs

This is the first attempt to qualify many of these semi-volatile DBPs in UK treated waters. A selection of 12 semi-volatile DBPs plus four THMs (Table 4.1) was made after determining the most prevalent species in 12 drinking US waters (Weinberg et al., 2002). SPE was used to concentrate up the DBPs to determine their presence in treated waters, offering an alternative extraction means to conventional LLE (Weinberg et al., 2002). With the SPE method used here, 100 mL of chlorinated water was concentrated to 2 mL providing a sufficient concentration factor of 50 fold to achieve low µg/L detection.

### 4.2.1 Materials and Methods

#### *4.2.1.1 Reagents and glassware*

The solvent used for SPE was MtBE (Ultra-Resi Analysed grade) from J.T. Baker (Phillipsburg, NJ, US). HPLC-grade methanol (Fisher Scientific, Pittsburgh, PA, US) was used to condition the cartridges. All the standards used here were commercially available (Table 4.1). The four THMs were available as Trihalomethanes Calibration Mix in a 1 mL ampoule. Four HANs, two HKs and one HNM were available as EPA 551B Halogenated Volatiles Mix in a 1 mL ampoule. All the other standards were available as individual species. The stock solutions were prepared in acetonitrile ($CH_3CN$) (Fisher Scientific, Pittsburgh, PA, US) and MtBE.

Table 4.1 Compound purity and suppliers

| Compounds | Stock solvent | Conc.[a] (µg/mL) | Purity (%) | Suppliers |
|---|---|---|---|---|
| **Trihalomethanes** | | | | |
| TCM | Methanol | 2000 | 97.5 | Sigma-Aldrich Ltd (St. Louis, MO, US) |
| BDCM | | | 98.9 | |
| DBCM | | | 96.9 | |
| TBM | | | 99.9 | |
| **Haloacetonitriles** | | | | Sigma-Aldrich Ltd (St. Louis, MO, US) |
| DCAN | Acetone | 2000 | 99.9 | |
| TCAN | | | 99.9 | |
| BCAN | | | 99.1 | |
| DBAN | | | 95.2 | |
| **Haloketones** | | | | |
| 1,1-DCP | Acetone | 2000 | 96.9 | |
| 1,1,1-TCP | | | 97.8 | |
| **Halonitromethanes** | | | | |
| TCNM (also called chloropicrin) | Acetone | 2000 | 99.9 | |
| DBNM | NA[b] | Neat | > 90 | Helix Biotech (Canada) |
| **Haloacetaldehydes** | | | | |
| DCA | NA[b] | Neat | > 90 | TCI America (Portland, OR, US) |
| TCA (also called chloral hydrate) | Acetonitrile | 1000 | 99.9 | Sigma-Aldrich Ltd (St. Louis, MO, US) |
| **Iodo-Trihalomethanes** | | | | |
| DCIM | NA[b] | Neat | > 90 | Helix Biotech (Canada) |
| BCIM | NA[b] | Neat | > 90 | |

[a] Concentration; [b] Not applicable.

Reagent water used in the preparation of calibration standards and blanks was prepared in the UNC laboratory using a water purification system (Pure Water Solutions,

Hillsborough, NC, US). The system filters chloraminated tap water to 1 µm, removes residual disinfectants, reduces TOC to less than 0.2 mg/L with activated carbon, and reduces conductivity to 18 MΩ-cm with mixed bed ion-exchange resins.

All non-volumetric glassware was detergent washed in a dishwasher, and then soaked in a 10% nitric acid bath. The glassware was removed and rinsed three times with deionised water and then placed in a 110°C oven over night or until thoroughly dry (about 4 hours). Volumetric glassware (pipettes, volumetric flasks, and graduated cylinders) was manually detergent-washed with tap water, rinsed three times with deionised water, then methanol, and allowed to dry on clean tissues (Kimwipes) in a dust-free environment. Caps and septa were soaked in a clean beaker filled with a mixture of deionised water and detergent for an hour or more, rinsed with deionised water, methanol, and then dried on a clean tissue.

#### *4.2.1.2 Preparation of standards*

The initial stock standard solutions for DBNM, DCA, DCIM and BCIM were first prepared in 10 mL acetonitrile from the neat compounds. Acetonitrile was recommended by Chinn et al. (2007) since the compounds have been observed to be stable in this solvent. The purity of these four compounds was below 95%; hence a correction factor was applied for the adjustment of the concentrations. For example 23.80 mg of DBNM was weighed, thus its accurate mass was actually 23.80 x 90% = 21.42 mg. The same calculations were applied for DCA, DCIM and BCIM. Therefore the initial stock solution concentrations for DBNM was 2142 µg/mL, 1760 µg/mL for DCA, 2304 µg/mL for DCIM and 2448 µg/mL for BCIM.

Stock solution 1 was prepared at a concentration of approximately 40 mg/L for each compound by transferring 100 µL of the THMs Calibration Mix pure material, 100 µL of the 551B Halogenated Volatiles Mix pure material, 200 µL of TCA pure material, 93.4 µL of DBNM initial stock solution, 113.5 µL of DCA initial stock solution, 87 µL of DCIM initial stock solution and 82 µL of BDIM initial stock solution into seven 5 mL volumetric flasks containing acetonitrile. Secondary standard solutions at 100 µg/L were prepared by diluting 25 µL of the stock solutions 1 in 10 mL volumetric flasks containing MtBE.

Initial standard solution and stock solution 1 were kept at -20ºC and were discarded after two weeks. Secondary standard solutions were made freshly on the day of analysis.

#### *4.2.1.3 Water sample preparation*

Treated water samples, used to determine the presence of the 16 DBPs, were geographically different. A lowland and an upland water were collected from South East England and northern England respectively. The treatment of the lowland water consisted of ozonation, coagulation, GAC and chlorination, whereas the treatment of the upland water was coagulation, sand filtration and chlorination. Both treated samples were collected prior to chlorination at the WTWs.

DBP-FP was carried out using an adaptation of procedure 5710 A in "Standard Methods for the Examination of Water and Wastewater" (APHA, 1992) and is described in more detail in Chapter 5, Section 5.2.3. An appropriate volume of chlorine dosing solution was added to a 100 mL bottle with PTFE-lined screw cap. Then the bottles were filled completely with water sample and were stored at 20 ºC for 3 days. No buffer was added to the samples. The final concentration of chlorine solution was 10 mg/L and was sufficient to form DBPs for the qualification work (Chapter 5, section 5.2.3).

#### *4.2.1.4 Method description*

SPE was performed using a commercially available 12-port Visiprep vacuum manifold and 1/8-inch Teflon tubing with weighted stainless steel ends (Supelco Chromatography, Bellafonte, PA, US). The SPE cartridge contained styrene divinyl benzene (DVB) polymeric beads (Strata; SDB-L; 500 mg, 3 mL, Phenomenex, US), and has been shown to be effective for sorbing all the DBPs investigated here (Chinn et al., 2007). Samples (100 mL) were placed in 125 mL conical flasks with the top of each sample vial wrapped with aluminum foil and the edges of the Teflon tubing sealed with a rubber band. The method is adapted from Weinberg et al. (2002) and Chinn et al. (2007) and is described in Figure 4.1.

Four 3 mL SPE cartridges were conditioned by adding 8 to 10 mL methanol, which was drained through the cartridge under vacuum. The methanol was then rinsed with 10 mL deionised water twice. The samples were then loaded into the cartridges headspace free using the Teflon tubing and the tube adapters. The flow rates were between 1 and 2 mL/min for all samples for complete passage through the sorbent. No quenching agent was used to dechlorinate the sample, thus the cartridges were then rinsed with 20 mL deionised water to eliminate remaining chlorine. The cartridges were then dried by setting up a vacuum pressure of 15 mm Hg for at least 20 minutes.

The samples were then eluted with 2 mL of MtBE into a 12 mm glass test tube. No vacuum was applied to this phase as it is important that the eluent spread throughout the cartridge. Manual pressure using a syringe was applied after 1 hour of contact with MtBE, to accelerate slightly the process of elution. The top layer of the test tube (MtBE) was then transferred to a 2 mL autosampler vial capped with a PTFE septum for analysis by GC/ECD.

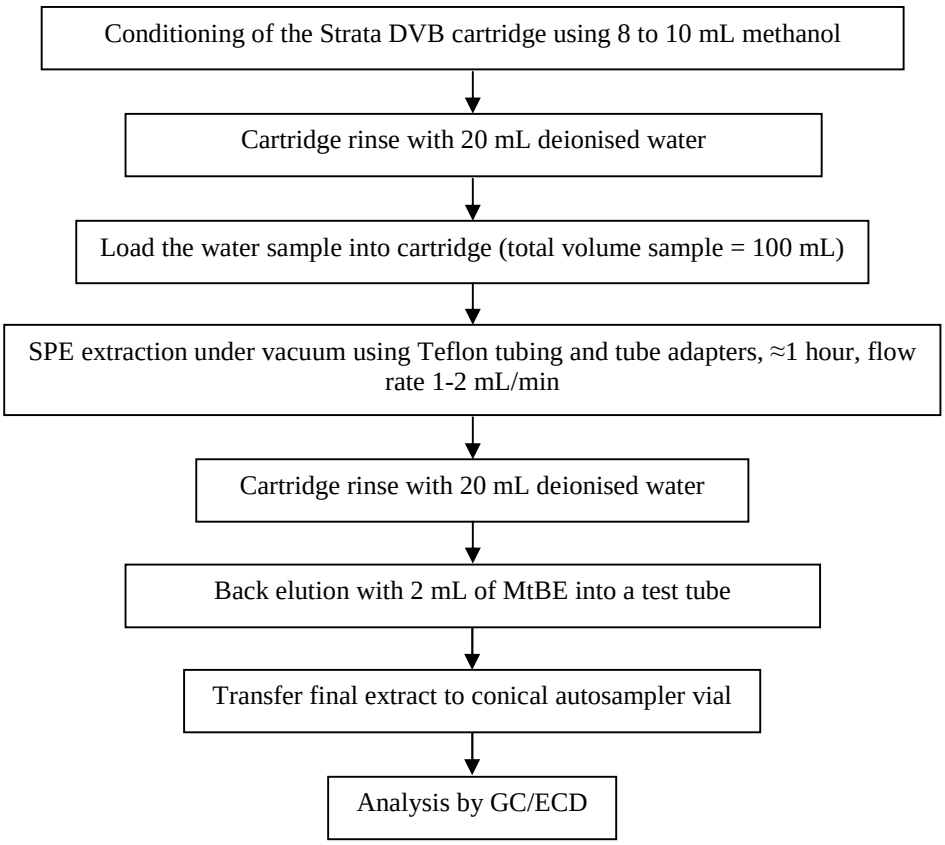



Figure 4.1 Summary of the SPE – GC/ECD method used for concentrating 16 DBPs in treated water (adapted from Weinberg et al., 2002 and Chinn et al., 2007)

#### *4.2.1.5 Instrument conditions*

Two gas chromatographs, using the same instrumental conditions, were used:

- A Hewlett Packard 5890 with a VF-1ms (30 m x 0.25 mm x 1 µm) column and
- A Hewlett Packard 6890 with a ZB-1701 (30 m x 0.25 mm x 1 µm) column.

A volume of 1 µL was injected splitless with the injector set at 180°C. The carrier gas was helium, set to a constant flow of 1 ml/min. An oven temperature program was used to maximise resolution of analytes. The GC oven temperature program was as follows: column temperature at 37°C, hold for 21 minutes, increase column temperature to 136°C at a rate of 5°C per minute and hold for 3 minutes, then finally increase column temperature to 250°C at a rate of 20°C per minute and hold for 3 minutes. The total run time was 52.50 minutes. The ECD was set at a temperature of 300°C. The make-up gas was nitrogen.

### 4.2.2 Results and Discussion

The SPE method was used for determining the presence of 12 semi-volatile DBPs plus four THMs in UK treated water. No calibration and quantification were attempted; hence, no method validation was carried out.

Initially, the THMs Calibration Mix, the 551B Halogenated Volatiles Mix, TCA, DBNM, DCIM and BCIM, all solutions at 100 µg/L in ultra pure water, were run with the GC/ECD fitted with the VF-1ms column. The orders of DBP elution for the THMs Calibration Mix and the 551B Halogenated Volatiles Mix (Figure 4.2) were determined by comparison to the confirmed orders of elution of the same compounds from the US nationwide DBP occurrence study by Weinberg et al. (2002), who used a DB-1ms (Figure 4.3). The two columns, VF-1ms and DB-1ms, have the same polarity (1ms – 100% dimethylpolysiloxane) but are produced by different manufacturers (DB - Agilent or VF - Varian). As seen below, the order of elution for the four THMs was TCM, BDCM, DBCM and TBM (Figure 4.2 A, Figure 4.3) and for the 551B Halogenated Volatiles MIX, the order was TCAN, DCAN, 1,1-DCP, TCNM, BCAN, 1,1,1-TCP and DBAN (Figure 4.2 B, Figure 4.3).

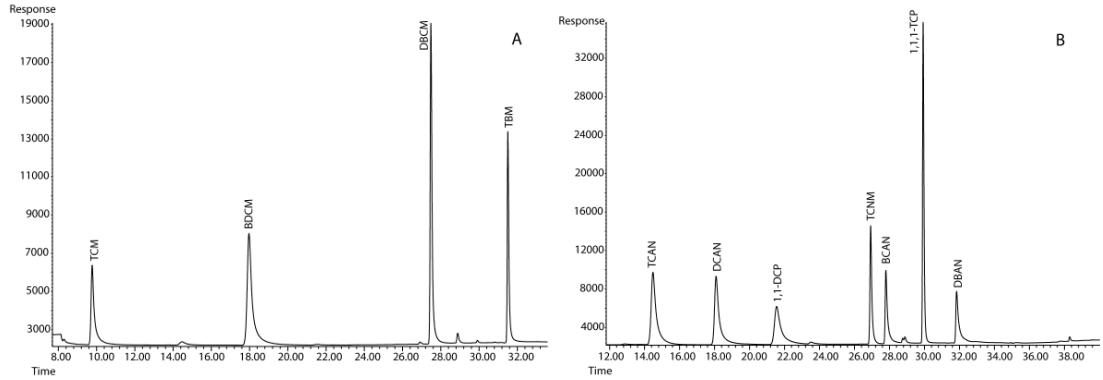



Figure 4.2 Order of elution of THMs (A) and 551B Halogenated Volatiles Mix (B) using the VF-1ms column (standard at 100 µg/L each – present study)

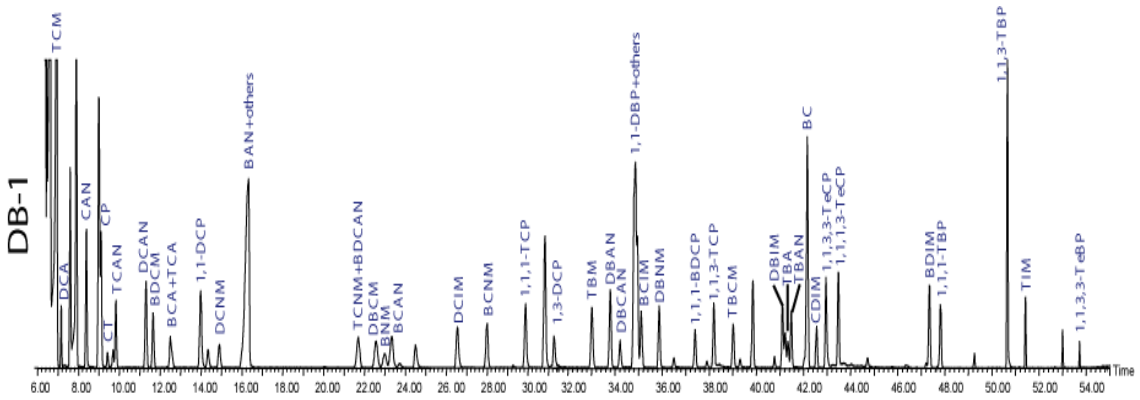



Figure 4.3 DB-1ms column performance using full DBP set from Weinberg et al. (2002) (16 targeted compounds + compounds not studied here)

Running the standards altogether showed that there were two co-eluting peaks; it was clear that BDCM and DCAN were not separated with the VF-1ms column (Figure 4.4 A), whereas they were with the DB-1ms column used by Weinberg et al. (2002) (Figure 4.3). This is believed to be due to the efficiency of the column; the column here had already been used for a few years and the inside stationary phase may have lost its efficiency. Hence working with the VF-1ms column, it was not possible to distinguish between DCAN and BDCM in the standards. Therefore it was decided to run the individual solutions on a second GC/ECD fitted with a ZB-1701 ((14%-cyanopropyl-phenyl)-methylpolysiloxane) column, which was available at UNC and can also be used for the quantification of HAAs (US EPA, 2003). The detection of BDCM and DCAN at two different retention times was possible (Figure 4.4 B). Nevertheless, the use of the

ZB-1701 column did not allow the detection of aldehydes; hence, it was not possible to detect DCA and TCA, but the use of the two columns was necessary to determine the presence of all of the compounds.

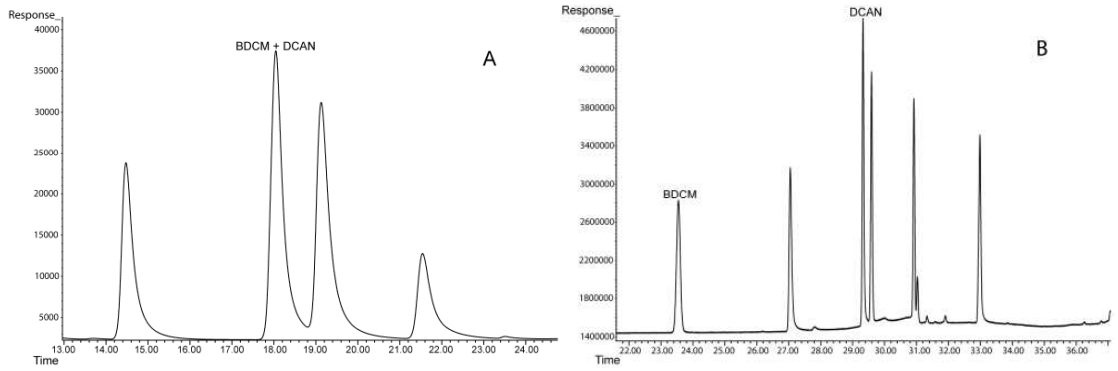



Figure 4.4 Elution of BDCM and DCAN with VF-1ms (A) and ZB-1701 (B)

Samples treated with SPE were run with both GC/ECD systems. The choice of three days for the chlorination of the two matrices was chosen to allow enough contact time with chlorine to form the optimum DBP concentration. We must also consider that the literature reported degradation of the DBPs with increasing reaction time with excess chlorine (Gurol et al., 1983; Reckhow and Singer, 1985; Ueno et al., 1996). Gurol et al. (1983) observed that 10% of 1,1,1-TCP degrades to chloroform during a contact time of 60 minutes. Reckhow and Singer (1985) found that 1,1-DCP degrades to form 1,1,1-TCP with excess chlorine, and Ueno et al. (1996) reported that the chlorination of DCAN resulted in the formation of HAAs (DCAA and TCAA) and TCM after 60 minutes contact time with chlorine. All the targeted compounds were detected here in the two matrices after three days of chlorination. It is noted that no quench agent was used to stop the reaction with chlorine and this was to avoid any artifact, such as further DBP degradation, associated with quenching agent and holding time (Gonzalez et al., 2000; Chinn et al., 2007). Samples were extracted directly at the end of the 72 hours incubation time.

When comparing with LLE, SPE eliminates the emulsion problems that can occur during LLE and used less solvent (Chinn et al., 2007). However, further work here will focus on treated water with low concentrations of organic matter and colour; hence it

was unlikely that a problem of emulsion would occur. The purpose of this work with SPE was to concentrate up the DBPs to determine their presence, but LLE has been reported to have better extraction efficiencies (Chinn et al., 2007). Moreover, LLE was cheaper, faster and was ultimately used for further analysis. Therefore no further work was undertaken with SPE.

### 4.2.3 Conclusion

The SPE method was used here as a preliminary study to determine the presence of 12 semi-volatile DBPs plus four THMs in two UK treated waters and this was successfully achieved. However it is believed that the LLE method could be faster and cheaper than the SPE method. Hence, further work to quantify the concentration of DBPs would use LLE.

## 4.3 LLE WITH GC/ECD METHOD VALIDATION

After determining the presence of 12 selected semi-volatile DBPs plus four THMs using SPE, the validation of LLE with analysis with GC/ECD is presented here. By comparison with the US nationwide occurrence study by Weinberg et al. (2002), it is expected the level of the 12 semi-volatile DBPs to be in the low range of µg/L and LLE is believed to be a rapid and cheap method that allows detection of DPBs at low µg/L levels.

### 4.3.1 Materials and Methods

#### *4.3.1.1 Reagent and glassware*

The solvent used for the LLE was MtBE, HPLC grade, the internal standard was 99% pure 1,2-dibromopropane and sulphuric acid was used to lower the pH. Copper sulphate was 99.995% pure, and sodium sulphate was 99% extra pure anhydrous and was baked overnight at 100°C before the extraction. All these chemicals were provided by Fisher Scientific (UK). The standards, their purity and their concentration were similar to these of the Section 4.2.1.1 Table 4.1, except that some of the suppliers differ. The

Trihalomethanes Calibration Mix, the EPA 551B Halogenated Volatiles Mix and the TCA were available from Sigma-Aldrich Ltd (UK). DBNM, DCIM and BCIM were as stated in Table 4.1. DCA was available from TCI Europe (Belgium). The stock solutions were prepared in acetonitrile (Fisher Scientific, UK) and MtBE. Ascorbic acid (Sigma-Aldrich Ltd, UK) was used as a quench agent and has been shown to not degrade any of the 16 DBPs (Chinn et al., 2007). Reagent water used in the preparation of calibration standards and blanks was prepared using PURELAB Ultra Genetic 18.2 MΩ-cm pure water (ELGA LabWater, UK).

All glassware was meticulously washed with deionised water, soaked in a 5% nitric acid solution for 12 hours, rinsed with deionised water three times and heated in a standard dryer until thoroughly dry. Because the accuracy of conical flasks can be affected by the standard dryer, they were placed on a drying rack until thoroughly dry.

#### *4.3.1.2 Preparation of standards*

Initial stock solutions and stock solution 1 at 40 mg/L were prepared as described in Section 4.2.1.2. Stock solution 2 at 4 mg/L was prepared by diluting exactly 1 mL of each solution into a 10 mL volumetric flask containing MtBE. Calibration standards at 0.5, 3, 7, 15, 50 and 100 µg/L were prepared by further dilution of the stock solution 2 in 100 mL volumetric flasks with pure water. Stock 2 and calibration standards were prepared freshly and discarded after use.

#### *4.3.1.3 Method description*

The extraction method was adapted from Krasner et al. (2001) and optimised the US EPA Method 551.1 (1995a). It is described in Figure 4.5.

A 30 mL sample was transferred to a 60 ml glass vial, then adjusted to a pH of 3.5 or less and extracted with 3 mL of MtBE containing an internal standard. The pH was checked with pH paper before the addition of MtBE. The solvent phase containing the DBPs was separated from the aqueous phase by addition of 10 g of sodium sulphate and 1 g copper sulphate. Then the sample was shaken manually for 3 to 5 minutes. The

layers were allowed to settle for 5 minutes and the top layer finally transferred to an autosampler vial and analysed with GC/ECD.

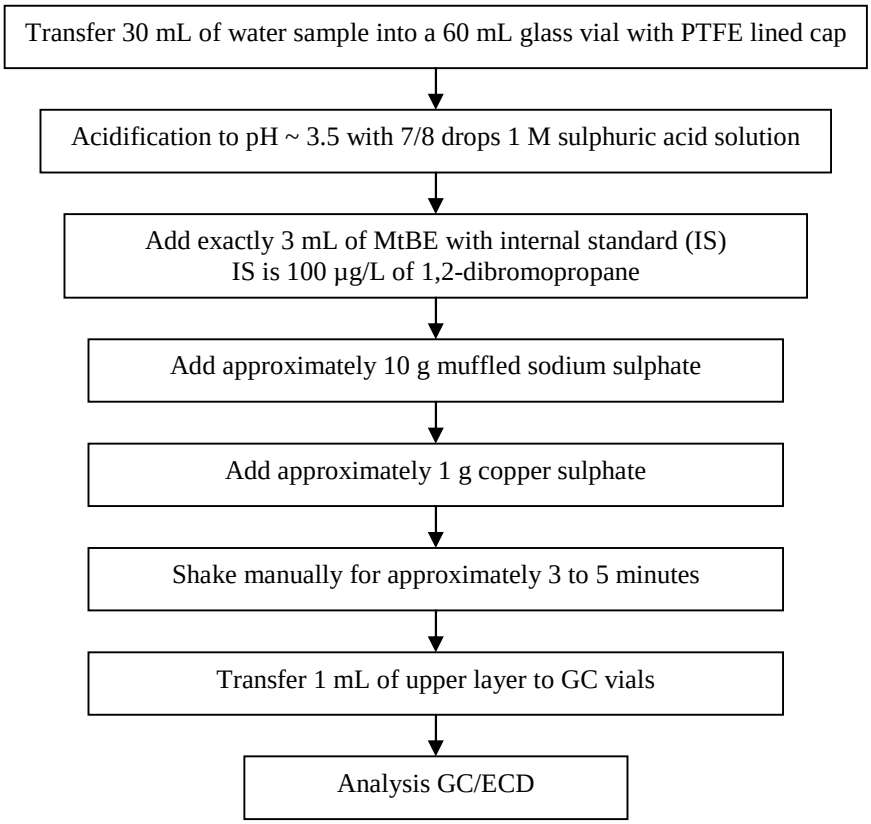



Figure 4.5 Summary of the LLE with GC/ECD method (adapted from Krasner et al., 2001)

*Optimisation of the US EPA Method 551.1 (1995a)*

The increased MtBE:water ratio in the method here (0.1:1 mL/mL) as compared to the Method 551.1 MtBE:water ratio (0.06:1 mL/mL) is believed to offer an advantage for the extraction of analytes with low partition coefficients (Gonzalez et al., 2000). Copper sulphate not used in the US EPA Method 551.1 (1995a) enhanced analyte recovery and aided in the extract transfer process (Weinberg et al., 2002).

#### *4.3.1.4 Instrument conditions*

DBP standards and samples were run with an Agilent 6890 GC/ECD. A volume of 1 µL was injected splitless with the detector set at 200°C. Separation was performed by a ZB-1ms column (30 m × 0.25 mm × 0.25 µm) with a helium carrier gas at a column flow rate of 1.0 mL/min. The initial oven temperature was 35°C and held for 22 minutes followed by a 10°C per minute temperature ramp to 145°C and held for 2 minutes and a final ramp of 20°C per minute ramp to 225°C and held for 10 minutes. The total run time was 49 minutes. The detector temperature was 290°C and the rate of collection data was 20 Hz.

#### *4.3.1.5 Method performance*

The average retention time for each DBP was determined with seven replicates of a derived 1.0 µg/L of each DBP and internal standard aqueous standard. The retention time precision was evaluated by calculating the relative standard deviation (RSD) as recommended by US EPA Method 551.1 (1995a). The RSD of the sample replicate analyses should be less than 15% and was calculated using the Equation 3.1 (Chapter 3).

Seven replicates of a derived 0.10 µg/L and 0.50 µg/L of each DBP aqueous standard were extracted and analysed over a period of three days for determining LODs. Ascorbic acid, which was the DBP preservative agent, was added to the standards at the same concentration as that used to quench the samples. LOD was calculated using the Equation 3.2 (Chapter 3). Blanks were not subtracted when performing LOD calculations.

The analyte recovery was determined by analysing two treated water samples spiked with three levels of DBPs. Fortifications were at 5, 25 and 75 µg/L. The recovery for each analyte was calculated using the Equation 3.3 (Chapter 3).

#### *4.3.1.6 Water samples*

The water samples are treated lowland and upland water as described in Section 4.2.1.3.

### 4.3.2 Results and Discussion

Before carrying out the quality controls prior to analyte quantification, the retention time of each solute was determined. As shown in the chromatograms (Figure 4.6), TCA, DCA, DBNM, BCIM and DCIM were available individually and their retention times were straightforward. On the other hand, THMs and the remaining species were available as mixes. By comparison with the US EPA Method 551.1 (1995a) and the US nationwide DBP occurrence study (Weinberg et al., 2002), which showed the order of elution of each species encompassed in both mixes using a DB-1ms column, the retention time identification was possible without further work.

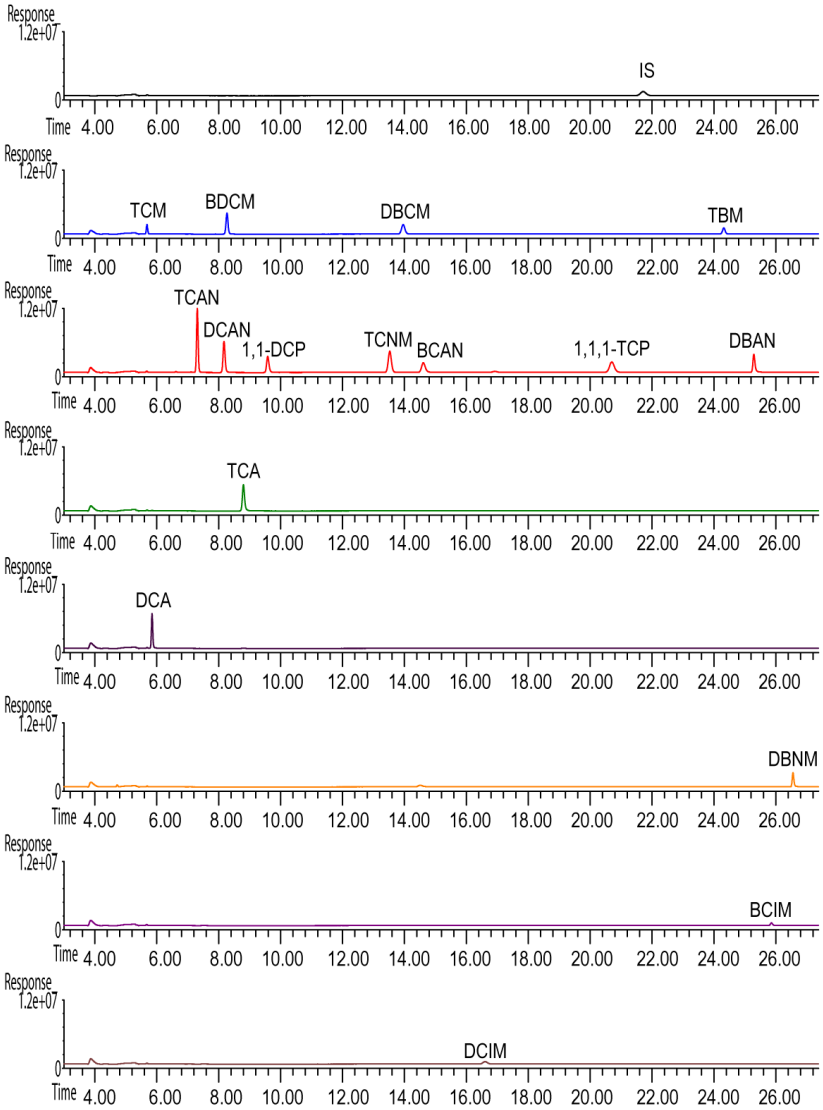



Figure 4.6 Individual chromatograms for semi-volatile contaminants and THMs (100 µg/L each DBP)

A typical chromatogram for 16 DBPs and internal standard were obtained by running a standard under the chromatographic conditions described in Section 4.3.1.4 (Figure 4.7). It has been found previously that BDCM and DCAN coeluted with a VF-1ms column. Here the ZB-1ms column used was relatively new and all the species were better separated. It should be noted that again BDCM and DCAN were not completely separated but were sufficiently separated to allow quantification.

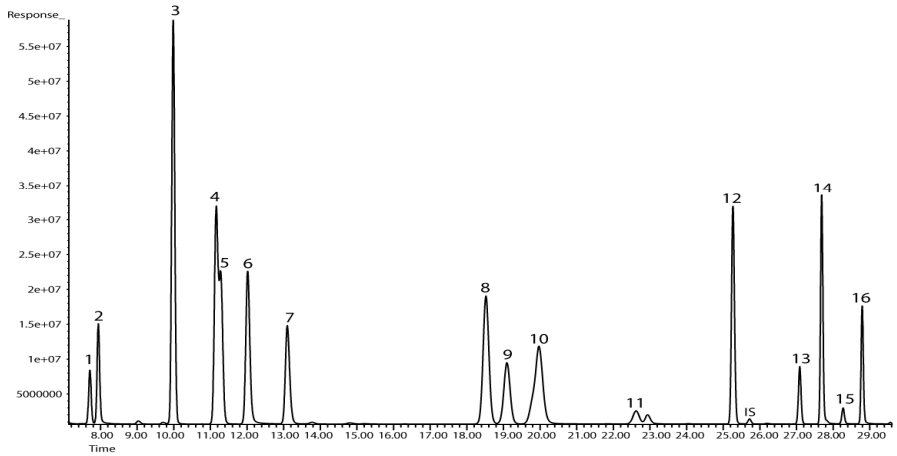



Figure 4.7 GC/ECD chromatogram for an extracted $DBP_{16}$ standard (100 µg/L) (see Table 4.2 for analyte identification)

The retention times for all 16 DBPs and internal standard are listed in Table 4.2. The RSD calculated for the retention times reported here were low, demonstrating good reproducibility of the method. To the knowledge of the author, this is the first published RSD data concerning the retention times of these compounds.

Table 4.2 Identification of the compounds and method performance

| Peak no. | Compound | Average tr[a] (min) | RSD[b] (%) | $R^2$ | Fortification level (µg/L) | Detection Limit[c] (µg/L) | MRL[d] (µg/L) |
|---|---|---|---|---|---|---|---|
| 1 | TCM | 7.72 | 0.058 | 0.999 | 0.50 | 0.088 | 0.264 |
| 2 | DCA | 7.95 | 0.052 | 0.993 | 0.50 | 0.124 | 0.371 |
| 3 | TCAN | 9.99 | 0.042 | 0.992 | 0.10 | 0.020 | 0.061 |
| 4 | DCAN | 11.17 | 0.060 | 0.997 | 0.10 | 0.019 | 0.057 |
| 5 | BDCM | 11.24 | 0.063 | 0.995 | 0.10 | 0.036 | 0.108 |
| 6 | TCA | 12.02 | 0.035 | 0.994 | 0.50 | 0.029 | 0.086 |
| 7 | 1,1-DCP | 13.12 | 0.030 | 0.998 | 0.10 | 0.029 | 0.086 |
| 8 | TCNM | 18.53 | 0.059 | 0.995 | 0.10 | 0.039 | 0.117 |
| 9 | BDCM | 19.10 | 0.045 | 0.997 | 0.10 | 0.049 | 0.148 |
| 10 | BCAN | 20.01 | 0.042 | 0.994 | 0.10 | 0.023 | 0.070 |
| 11 | DCIM | 22.64 | 0.067 | 0.996 | 0.10 | 0.086 | 0.257 |
| 12 | 1,1,1-TCP | 25.28 | 0.013 | 0.995 | 0.10 | 0.089 | 0.268 |
| 13 | TBM | 27.10 | 0.037 | 0.999 | 0.10 | 0.095 | 0.284 |
| 14 | DBAN | 27.71 | 0.009 | 0.944 | 0.10 | 0.014 | 0.041 |
| 15 | BCIM | 28.28 | 0.015 | 0.996 | 0.10 | 0.108 | 0.324 |
| 16 | DBNM | 28.81 | 0.012 | 0.998 | 0.10 | 0.059 | 0.178 |
| IS | IS[e] | 25.72 | 0.008 | NA[f] | NA[f] | NA[f] | NA[f] |

[a] The average retention time corresponds to the average of seven injections; [b] Corresponds to the relative standard deviation and must be less than 15% according to US EPA Method 551.1 (1995a); [c] Fortified waters were extracted and analysed over 3 days for seven replicates; [d] Corresponds to the minimum reporting level and is the threshold expected for accurate quantification in an unknown sample. It has to be at least three times the limit of detection; [e] 1,2-dibromopropane; [f] Not applicable.

To determine whether pure water could be used as a matrix for the calibration and validation work, analyte absolute recovery was calculated in pure water, lowland and upland water, using the calculation as in Section 4.3.1.5, Equation 3.3. Analyte absolute recovery is based on the true response (i.e. y axis of chromatogram) and does not involve calibration or quantitation. Thus analyte absolute recovery was assessed in pure water and treated waters, by spiking 30 µg/L of DBPs in each matrix. Absolute recoveries were low (40 to 60% for all matrices), but the RSD of the recovery between matrices was less than 10%. Thus pure water was used for calibration work.

Calibration was performed by extracted procedural standards, i.e. fortified pure water, by the procedure described in Section 4.3.1.3. Although the US EPA Method 551.1 (1995a) recommended five calibration standards, here it was decided to work with six calibration points. Some of the compounds analysed here are not encompassed in the US EPA Method 551.1 (1995a), and their behaviour at low range and high range of concentrations was not known. Six calibration standards enabled coverage of low and high concentrations and were 0.5, 3, 7, 15, 50 and 100 µg/L. The calibration curves

were generated by plotting area ratios ($A_{DBP}/A_{IS}$) against the concentration $C_{DBP}$ of the six calibration standards (Figure 4.8)

where: $A_{DBP}$ = the peak area of the DBP

$A_{IS}$ = the peak area of the internal standard

$C_{DBP}$ = the concentration of the DBP.

A linear calibration curve was obtained for each of the 16 DBPs (Figure 4.8) and no DBP was detected in pure water free of DBP spikes. The coefficients of determination of linear regression are reported in Table 4.2 and were all above 0.944.

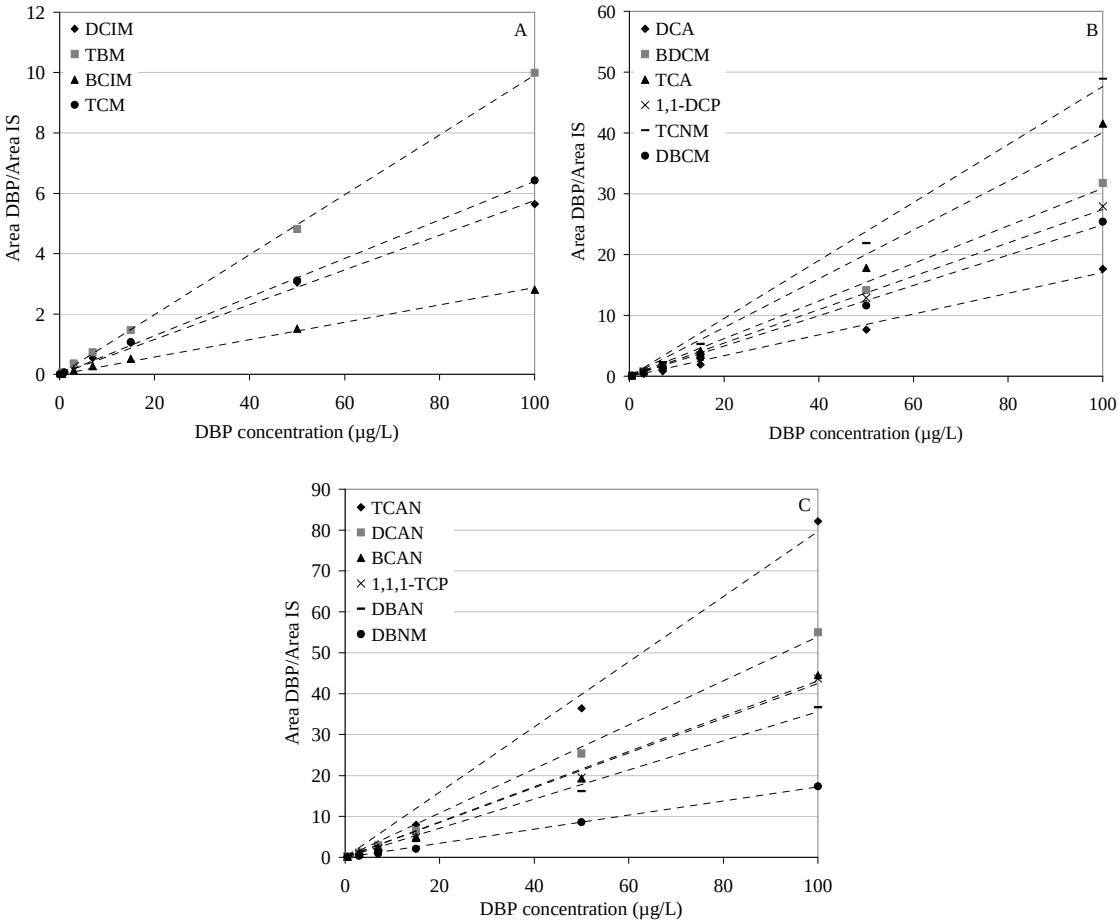



Figure 4.8 Calibration curves for (A) DCIM, TBM, BCIM and TCM – (B) DCA, BDCM, TCA, 1,1-DCP, TCNM and DBCM – (C) TCAN, DCAN, BCAN, 1,1,1-TCP, DBAN and DBNM – Concentration: 0.5, 3, 7, 15, 50 and 100 µg/L

The LOD (Table 4.2) for the 16 DBPs were between 0.014 and 0.124 µg/L. Detection limits for TCM and DCIM were 0.088 and 0.086 µg/L respectively and were comparable to a study by Gonzalez et al. (2000), where they found LOD of 0.07 and 0.09 µg/L respectively in a mixture of DBPs. The 14 remaining DBPs showed better LOD than these reported by the same study. The US EPA Method 551.1 (1995a) showed better recovery for every species, with LOD between 0.001 and 0.055 µg/L for 12 species (4 THMs, 4 HANs, 2 HKs, TCNM and TCA). The difference is believed to be due to the extent of replication. Here seven replicates were used for determining LOD, whereas eight replicates were utilised in the US EPA Method 551.1 (1995a) and six replicates were used in the study of Gonzalez et al. (2000), modifying the Student t value used in the calculation of the LODs. The total LOD here was 0.907 µg/L. In relation to LOD, the minimum reporting level (MRL) for each DBP was calculated (Table 4.2). The MRL, which is at least three times the LOD, corresponds to the threshold expected for accurate quantification in an unknown sample. Each DBP could be well quantified below 0.4 µg/l. It was decided to accept MRL below 0.5 µg/L considering the good accuracy of the calibration curves.

Analyte recoveries exhibited bias in both water samples (Table 4.3 and Table 4.4). The guideline provided by the US EPA Method 551.1 (1995a) recommends that recoveries should range between 80 and 120%. However, it was decided here to accept 70 to 130% recovery for the high levels of fortification, and 50 to 150% for the low level of fortification, as these are the acceptable values for HAAs (US EPA, 2003). Furthermore, the preparation of the samples here differs from the US EPA Method 551.1 (1995a), and the method exhibited a broader range of recovery which is explained later in the text.

Table 4.3 Spike recovery in lowland water fortified with DBPs

| Compounds | Fortification at 5 µg/L | | Fortification at 25 µg/L | | Fortification at 75 µg/L | |
|---|---|---|---|---|---|---|
| | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) |
| THMs | | | | | | |
| TCM | UTR[c] | UTR[c] | UTR[c] | UTR[c] | **162**[b] | 102.7 |
| BDCM | 73 | 5.8 | 75 | 5.6 | 92 | 3.0 |
| DBCM | 85 | 3.5 | 81 | 4.8 | 91 | 3.2 |
| TBM | 113 | 1.8 | 94 | 3.5 | 93 | 2.2 |
| HANs | | | | | | |
| DCAN | 73 | 4.4 | 74 | 6.0 | 83 | 12.0 |
| TCAN | **10**[b] | 60.0 | **8**[b] | 116.0 | **17**[b] | 83.5 |
| BCAN | 84 | 1.0 | 81 | 3.0 | 88 | 5.5 |
| DBAN | 72 | 3.3 | 78 | 4.0 | 92 | 3.8 |
| HKs | | | | | | |
| 1,1-DCP | 86 | 1.1 | 83 | 2.1 | 88 | 1.2 |
| 1,1,1-TCP | 57 | 3.2 | **57**[b] | 10.4 | **60**[b] | 31.0 |
| HNMs | | | | | | |
| TCNM | **37**[b] | 50.2 | **61**[b] | 18.3 | 73 | 22.0 |
| DBNM | 54 | 49.1 | 74 | 13.5 | 90 | 8.0 |
| HAs | | | | | | |
| DCA | ND[d] | ND[d] | ND[d] | ND[d] | **48**[b] | 5.5 |
| TCA | ND[d] | ND[d] | ND[d] | ND[d] | **66**[b] | 11.7 |
| i-THMs | | | | | | |
| DCIM | 124 | 8.7 | 95 | 10.1 | 86 | 6.5 |
| BCIM | 127 | 10.6 | 90 | 16.0 | 86 | 9.8 |

[a] Corresponds to the relative standard deviation and must be less than 15% according to US EPA Method 551.1 (1995a); [b] Corresponds to biased values; [c] Unable to resolve; [d] Not detected.

Table 4.4 Spike recovery in upland water fortified with DBPs

| Compounds | Fortification at 5 µg/L | | Fortification at 25 µg/L | | Fortification at 75 µg/L | |
|---|---|---|---|---|---|---|
| | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) | Mean recovery (%) | RSD[a] (%) (n = 3) |
| THMs | | | | | | |
| TCM | UTR[c] | UTR[c] | UTR[c] | UTR[c] | 99 | 72.6 |
| BDCM | 74 | 12.2 | 70 | 14.3 | 89 | 7.3 |
| DBCM | 83 | 4.6 | 81 | 5.0 | 92 | 5.2 |
| TBM | 110 | 3.6 | 94 | 3.4 | 93 | 3.6 |
| HANs | | | | | | |
| DCAN | 76 | 4.4 | 84 | 2.3 | 93 | 1.4 |
| TCAN | **45**[b] | 24.6 | **56**[b] | 16.8 | 83 | 14.2 |
| BCAN | 87 | 12.8 | 87 | 1.1 | 96 | 2.9 |
| DBAN | 72 | 6.6 | 80 | 3.4 | 94 | 3.8 |
| HKs | | | | | | |
| 1,1-DCP | 86 | 2.2 | 86 | 1.0 | 92 | 1.7 |
| 1,1,1-TCP | 74 | 2.3 | 80 | 1.0 | 92 | 2.0 |
| HNMs | | | | | | |
| TCNM | **42**[b] | 43.3 | **68**[b] | 11.7 | 89 | 8.4 |
| DBNM | **15**[b] | 4.0 | **62**[b] | 18.6 | 87 | 10.9 |
| HAs | | | | | | |
| DCA | **42**[b] | 24.2 | **47**[b] | 4.0 | **61**[b] | 11.1 |
| TCA | 55 | 13.4 | **67**[b] | 1.5 | 84 | 4.0 |
| i-THMs | | | | | | |
| DCIM | 123 | 9.7 | 93 | 8.0 | 87 | 10.0 |
| BCIM | 120 | 19.2 | 89 | 18.4 | 87 | 12.5 |

[a] Corresponds to the relative standard deviation and must be less than 15% according to US EPA Method 551.1 (1995a); [b] Corresponds to biased values; [c] Unable to resolve.

The US EPA Method 551.1 (1995a) recommends adjusting the pH of the matrix to between 4.5 and 5.5 when collecting samples before the extraction outlined in Figure 4.5. Here the pH of both waters has not been adjusted before the extraction and was slightly basic and neutral (7.9 and 6.7 for lowland and upland water respectively). As a result, TCAN was biased in both waters, with poorer recovery in the lowland water. TCAN can undergo base-catalysed hydrolysis at pH higher than 5.5 (Croué and Reckhow, 1989), and this is believed to be the cause. 1,1,1-TCP and TCNM were also found to be biased in the lowland water and this is mainly attributed to the matrix effect. HNMs were biased in the upland water for concentration ≤ 25 µg/L. Despite their low recoveries, HNMs were better recovered in the lowland water. Finally HAs were biased in both waters. At levels ≤ 25 µg/L, DCA and TCA could not be detected in the lowland water. Chinn et al. (2007) reported that TCA degraded almost completely at pH 8.3 after

being spiked at 30 µg/L for 95 minutes, and DCA showed degradation of 20%, whereas at pH 3.5, DCA and TCA were stable for more than two weeks. Hence the bias exhibited for DCA and TCA is likely to be caused by the initial pH of the water. Although it is also thought that the matrix will have an impact.

It has been demonstrated by the US EPA Method 551.1 (1995a) and Gonzalez et al. (2000) that the extraction procedure gives good recoveries when pH is below 5.5. Hence no further work was undertaken here for analyte recovery.

TCM could not be included when the concentration was ≤ 25 µg/L due to contamination (Figure 4.9). The contamination peak had a similar response to the TCM spike response at 5 and 25 µg/L, making the recovery percentage impossible to determine. Furthermore recovery observed at 75 µg/L exhibited bias and/or very high RSD and this is believed to be due to the contamination and not the matrix impact. Indeed previous work (Parsons et al., 2009) assessing the recovery of TCM in the same waters with the US EPA Method 551.1 (1995a) found values of 86 to 134% at low levels, concluding no bias for TCM in both waters. The origin of the contamination has not been determined. Nevertheless, because LOD could be detected and a calibration curve could be drawn, no further work was undertaken for analyte recovery of TCM.

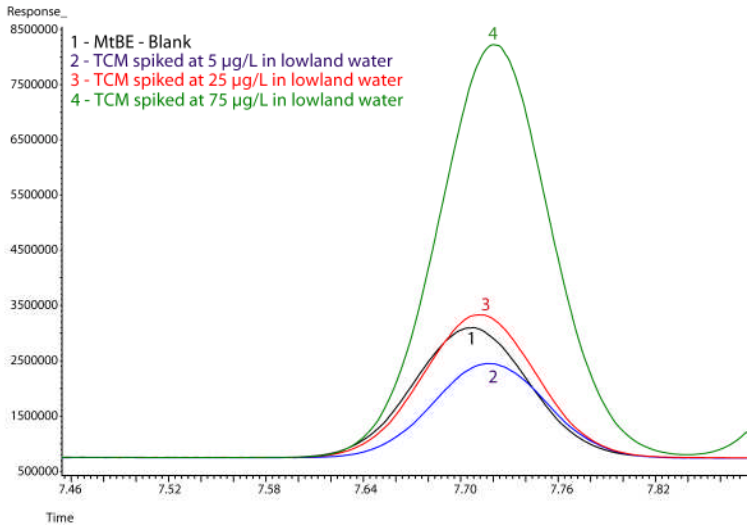



Figure 4.9 Contamination and TCM peaks while working on recovery in lowland water

### 4.3.3 Limitations

Despite rapid sample preparation and good limits of detection, a few parameters must be considered while determining the level of the 12 semi-volatile DBPs plus four THMs with LLE. First of all it is recommended to acidify the samples as soon as the reaction is finished and to extract and process the samples as soon as they have been quenched to avoid any possible degradation due to base-catalysed hydrolysis. The quenching agent can also be responsible for degradation (Gonzalez et al., 2000) and here we quenched with ascorbic acid, which has been shown not to degrade the 16 DBPs (Chinn et al., 2007). However, it is recommended for further work that could include more DBPs, such as bromopicrin or tribromoacetonitrile, etc. to investigate the use of ammonium chloride as secondary quenching agent because these DBPs are not stable in the presence of ascorbic acid (Chinn et al., 2007).

### 4.3.4 Conclusion

The method validated here was found to be both reproducible and precise with some bias. Linear calibration curves were reported for each DBP. Spike recovery calculations showed biased analytes in both waters and this was attributed to the matrix impact and the initial pH of the water samples. Hence the investigation of accuracy, precision, working range, selectivity showed the method to be reliable and the limit of detection of 0.17 µg/L for each DBP was met, validating the method for further work.

## 4.4 CHAPTER SUMMARY

The results presented here showed that 12 semi-volatile DBPs, plus four THMs were present in two different UK treated waters, when concentrated by a factor of 50 using SPE. Nevertheless, the LLE method requires less time for the sample preparation and it is cheaper compared to SPE. Hence, LLE was chosen for the quantification of these 16 DBPs. Low µg/L concentrations of these compounds in treated water were expected and the LLE method allowed quantification at these levels. In addition LOD, detected for each DBP, was found to be satisfactory, validating the method. Bearing in mind that limitations of the method concern the pH and the quenching agent, it is recommended to

lower the pH to 4.5 – 5.5 to avoid any possible DBP degradation. It is also important to choose a quenching agent that is inert toward the DBPs.

# Chapter 5

# COMPARISON OF THE DBP-FP OF UK TREATED WATERS EXPOSED TO CHLORINE AND MONOCHLORAMINE

## 5.1 INTRODUCTION

Drinking water DBPs result from the reaction of chlorine NOM and/or bromide/iodide present in drinking water supplies (Rook et al., 1974). THMs are the only regulated DBPs in the UK and it is required by law that the sum of four THMs does not exceed 100 µg/L with a frequency of sampling dependent on the population size. HAAs are often found to be as prevalent as THMs but are currently not regulated in the UK. However, the European Union is considering regulating the nine HAAs at 80 µg/L (Cortvriend, 2008) and as such there is growing interest in the levels of these compounds found in UK drinking waters and how best to control them.

In order to comply with these proposed regulations, there has been an increasing interest in using monochloramine as a secondary disinfectant because of reduced DBP formation and its ability to provide residuals in water distribution systems. Monochloramine is known to only form trace amounts of THMs and HAAs. However, the formation of DXAAs, although, generally lower than with chlorine, can still reach significant levels depending on the dose, chlorine to ammonia ratio, pH and other conditions (Diehl et al., 2000; Hua and Reckhow, 2007). The use of monochloramine may also lead to an increase in other DBPs such as HANs and i-THMs (Krasner et al., 1989; Bichsel and Von Gunten, 2000). HANs and i-THMs are two unregulated classes of semi-volatile DBPs also present in disinfected waters alongside other unregulated DBPs including HNMs, HAs and HKs (Krasner et al., 2006). These semi-volatile DBPs are of interest because of their toxicity. HANs have been reported to be genotoxic and potentially carcinogenic for human health and HKs exerted carcinogenic or mutagenic effects in mice (Bull and Robinson, 1986; Daniel et al., 1986). Plewa et al. (2004) found HNMs to be toxic in CHO cells and Richardson (2003) suggested that i-THMs

could be more toxic than their brominated and chlorinated analogues.

Past research has established that levels of HAAs and THMs in chlorinated waters vary according to the levels of their precursors. High NOM concentrations have generally been associated with high HAA and THM concentrations (Liang and Singer, 2003; Sharp et al., 2006a) and nitrogenous precursors from algae or effluent organic matter (EfOM) have been related to nitrogenous DBPs, such as HANs (Oliver et al., 1983). The presence of bromide in water will also affect the concentration of DBPs as will other factors such as the disinfectant dose applied, the pH, the temperature of the water samples and the reaction time of disinfectant in water (Singer et al., 2002). To better control and understand the formation of DBPs in water samples, the use of FP tests have been widely used (Zhang et al., 2000; Liang and Singer, 2003; Ates et al., 2007; Krasner et al., 2007). FP tests are usually conducted with controlled pH, controlled temperature and relatively high chlorine concentration dosed for a long contact time in order to maximise DBPs formation (Krasner et al., 2007).

Because HAAs are not routinely measured in the UK, there is currently little information concerning their levels, their formation route and their relation to other DBPs. Furthermore an insight into semi-volatile DBPs was of interest, because of their toxicity and their presence in disinfected waters using chlorine or monochloramine (Krasner et al., 2006). To have a better understanding of HAAs, THMs and semi-volatile DBPs in UK treated waters, their formation was evaluated under controlled conditions. The use of FP tests allowed a direct comparison between the use of chlorine and monochloramine and the impact the change of disinfectant had on the DBP levels.

The objectives of the work presented in this chapter were (1) to determine the relative distribution and speciation of DBPs from treated water using FP tests, (2) to compare the formation of DBPs with chlorine or monochloramine and (3) to identify any relationships between water sources and DBPs. Here 11 WTWs across England and Wales have been surveyed to give a wide range of water sources as well as different water characteristics. The DBPs included $THM_4$, $HAA_9$ but also four HANs (DCAN, TCAN, BCAN and DBAN), two HKs (1,1-DCP and 1,1,1-TCP), two HAs (DCA and TCA), two HNMs (TCNM and DBNM) and two i-THMs (DCIM and BCIM).

## 5.2 MATERIALS AND METHODS

### 5.2.1 Water sample collection

Treated water samples were collected in July 2008 from 11 WTWs (Table 5.1), selected by the water companies and spread geographically across England and Wales. Samples were collected at the end of treatment processes but prior to disinfection. The processes from each works are outlined in Table 5.1. All samples were collected in polyethylene or glass 1L bottles and shipped to Cranfield laboratories. All samples were kept refrigerated at 5°C until analysis. Analyses were conducted within 7 to 15 days after the samples were received.

### 5.2.2 Water sample characterisation

#### *5.2.2.1 pH*

pH was measured with a Jenway 3310 pH meter, calibrated each day of use with buffer solution pH 4 (phthalate), pH 7 (phosphate) and pH 10 (borate) (Fisher Scientific, UK).

#### *5.2.2.2 Non purgeable organic carbon (NPOC)*

NPOC was measured using a Shimadzu TOC-5000A analyser (Shimadzu, Milton Keynes, UK). Samples were acidified and purged with air to convert the inorganic carbon to $CO_2$. The total carbon (TC) was then measured and was referred to as NPOC. The TC standard was made by dissolving 2.125 g potassium hydrogen phthalate in 1L ultra pure water.

The standard had a concentration of 1000 mg/L and working standards were diluted to the appropriate concentration with pure water. The machine was calibrated on the day of analysis. The analyser took up to five replicates and reported an average of three given that the coefficient of variance was not greater than 2%. The analyser was recalibrated if the value of the standards were not within 10% of the expected value.

#### *5.2.2.3 UV / SUVA*

UV absorbance at 254 nm was measured using a Jenway 6505 UV/VIS spectrophotometer (Patterson Scientific Ltd., Luton, UK), calibrated using pure water as a blank.

SUVA (L/m-mg C) was calculated as the ratio of UV absorbance at 254 nm (1/m) to NPOC (mg C/L).

#### *5.2.2.4 Bromine and iodine measurement*

Samples were analysed using an Elan 9000 inductively coupled plasma mass spectrometry (ICP/MS) from Perkin Elmer (UK). The ICP/MS detects only elemental ions. The concentration of each element is determined by comparing the counts for a selected isotope to an external calibration curve generated for that element. For bromine, a calibration curve was set up from 10 to 500 µg/L and for iodine, 0.5 to 20 µg/L. Liquid samples were introduced to the ICP/MS by a peristaltic pump whereupon samples were nebulised and sprayed into the instrument to meet the high temperature plasma. For each sample, three replicates were analysed at a rate of 60 sweeps per reading. The integration time was set at 3000 ms and the dwell time 50 ms per atomic mass unit. The scan mode was peak hopping and the carrier gas was argon set at 1 mL/min.

### 5.2.3 DBP-FP

#### *5.2.3.1 Chlorine and monochloramine solution*

Preparation and determination of the chlorine solution was carried out using the procedure 4500-Cl B. Iodometric Method I in “Standards Methods for the Examination of Water and Wastewater” (APHA, 1992).

Preparation and determination of the monochloramine solution was carried out using the method 4500-Cl F. DPD Ferrous Titrimetric Method (APHA, 1992).

#### *5.2.3.2 Buffer*

A stock solution of sodium phosphate dibasic ($Na_2HPO_4$, Fisher Scientific, UK) at 1/15 M and potassium acid phosphate ($KH_2PO_4$, Fisher Scientific, UK) at 1/15 M was prepared respectively by dissolving 4.733 g in 0.5 L of ultra pure water and 4.540 g in 0.5 L of ultra pure water. A buffer at pH 7.2 was making up by adding 27 mL of the $KH_2PO_4$ stock solution to 73 mL of $Na_2HPO_4$. The buffer was made fresh when the pH fell below 0.2 pH units of the expected value.

#### *5.2.3.3 Quench solutions*

Ammonium chloride at a concentration of 100 mg/L was used to quench chlorine and monochloramine residual while not degrading HAAs, in particular $HAA_3$ (BDCAA, DBCAA and TBAA) (Singer et al., 2002). This solution was discarded after two weeks.

Ascorbic acid at a concentration of 35 mg/L was used to quench chlorine and monochloramine residual in THM and semi-volatile DBP samples. The choice is based on the fact that ascorbic acid has been shown not to degrade any of these 16 DBPs (Chinn et al., 2007). This solution was discarded after two weeks.

HAA, THM and the semi-volatile DBP samples were extracted immediately after incubation time to avoid possible artifacts associated with quenching agents and holding times.

#### *5.2.3.4 Samples exposed to chlorine and monochloramine*

For DBP-FP tests conducted in the presence of chlorine, samples were chlorinated at pH 7.2; based on the NPOC level in each sample, chlorine:NPOC ratio was 3:1 on a weight basis. A 100 mL bottle was partly filled with the water sample, the buffer and the chlorine solution were added and the bottle was filled completely and capped headspace free with a PTFE-lined cap. Samples were placed for 24 hours at 20°C in the dark. At the end of the incubation period the chlorine residual was quenched with 136 µL of ammonium chloride for HAA samples and with 50 µL of ascorbic acid for the THM and the semi-volatile DBP samples.

DBP-FP tests conducted in the presence of monochloramine were carried out using preformed monochloramine created by mixing aqueous ammonium sulphate and sodium hypochlorite solutions (HOCl) in accordance with Diehl et al. (2000). A chlorine to nitrogen mass ratio of 3:1 was used in all samples and addition of monochloramine was based on the NPOC level, with combined chlorine:NPOC ratio of 3:1 by weight. The procedure of monochloraminated samples was the same as that for chlorinated samples and the quench agents were identical.

### 5.2.4 Sample analytical methods

HAA samples were extracted with a method reported by Tung et al. (2006) and is a modified version of US EPA Method 552.2 (1995). The method description and the instrumentation conditions are reported in Chapter 3 Section 3.3.

THMs and the semi-volatile DBPs were extracted with an adapted method from Krasner et al. (2001). The method description and the instrumentation conditions are reported in Chapter 4 Section 4.3.

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Water characterisation

Samples of treated waters collected from drinking WTWs across England and Wales were analysed for pH, NPOC, UV, bromine and iodine. These results are presented along with calculated SUVA values (Table 5.1). The average NPOC concentration was 1.6 mg/L with the highest value (3.7 mg/L) found in LR and the lowest concentration (0.2 mg/L) in B1. The NPOC concentration of the lowland rivers (mean of 1.7 mg/L) was similar to that measured in the upland reservoirs (mean of 1.5 mg/L).

SUVA is a useful parameter when assessing NOM as it indicates the UV-absorbing chromophores (aromatic carbon moieties) from molecules and is strongly linked to the precursor polarity and hence DBP concentrations (Edzwald and Tobiason, 1999; Hwang et al., 2001). SUVA values calculated here ranged from 1.5 L/m-mg C (B1) to 5.4 L/m-mg C (UR3). L1 and UR3, with low NPOC values (1.2 and 1.1 mg/L respectively), had high SUVA values of 4.6 and 5.4 L/m-mg C respectively, which indicate that the NOM

was hydrophobic in character. Previously, hydrophobic NOM has been reported to preferentially form THMs and TXAAs (Hwang et al., 2001). In general, the upland waters had greater SUVA values than the lowland waters and boreholes (average of 3.5, 1.9 and 1.7 L/m-mg C respectively).

Table 5.1 List of WTWs, sources and water characteristics

| Work ref. | Work description | pH | NPOC (mg/L) | $UV_{254}$ (1/m) | $SUVA_{254}$ (L/m-mg C) | Bromine (µg/L) | Iodine (µg/L) |
|---|---|---|---|---|---|---|---|
| BOREHOLE (B) | | | | | | | |
| B1 | *Sampling point:* Post filter<br>*Main process:* Filtration | 7.8 | 0.2 | 0.4 | 1.5 | 275 | 3.5 |
| B2 | *Sampling point:* Post membrane prior to superchlorination<br>*Main process:* Membrane filtration with pre-oxidation | 7.2 | 1.2 | 2.2 | 1.8 | 42 | 6.9 |
| LAKE (L) | | | | | | | |
| L1 | *Sampling point:* Post membrane<br>*Main process:* Membrane filtration | 5.9 | 1.2 | 5.5 | 4.6 | 31 | 1.3 |
| L2 | *Sampling point:* Post filter<br>*Main process:* Coagulation/Direct filtration | 6.8 | 1.2 | 3.4 | 2.7 | 75 | 16.7 |
| LOWLAND RESERVOIR (LR) | | | | | | | |
| LR | *Sampling point:* Post GAC<br>*Main process:* Ozone/coagulation /GAC | 7.8 | 3.7 | 5.8 | 1.6 | 209 | 8.9 |
| UPLAND RESERVOIR (UR) | | | | | | | |
| UR1 | *Sampling point:* Post sand filtration<br>*Main process:* Coagulation | 7.4 | 1.6 | 4.2 | 2.6 | 44 | 0.9 |
| UR2 | *Sampling point:* Post filter<br>*Main process:* Coagulation/filtration | 8.9 | 1.7 | 4.1 | 2.4 | 18 | 0.9 |
| UR3 | *Sampling point:* Post slow sand filter<br>*Main process:* Direct filtration | 6.2 | 1.1 | 5.9 | 5.4 | 29 | 0.9 |
| LOWLAND RIVER (BR) | | | | | | | |
| BR1 | *Sampling point:* Post GAC<br>*Main process:* Coagulation/GAC | 5.5 | 2.2 | 5.3 | 2.4 | 14 | 0.9 |
| BR2 | *Sampling point:* Post GAC<br>*Main process:* Coagulation/GAC | 7.5 | 1.6 | 2.9 | 1.8 | 310 | 6.3 |
| BR3 | *Sampling point:* Post GAC<br>*Main process:* Coagulation/GAC | 7.2 | 1.4 | 2.4 | 1.7 | 108 | 3.0 |

ref. - reference

No specific trends were observed between the water treatment processes used and the treated water SUVA values. The two waters with the highest SUVA (L1 and UR3) were treated with direct filtration, not coagulation, which is more effective towards removal of hydrophobic material (Sharp et al., 2006a).

The level of bromine, which is assumed here to be mainly bromide, ranged from 14 to 310 µg/L (Table 5.1), with an average concentration of 105 µg/L. This is in line with the levels reported by Amy et al. (1994) who reported that typical concentrations of bromide in natural waters ranging from 30 to 200 µg/L, with an average of 100 µg/L. The highest concentrations were found in B1, LR, BR2 and BR3. It is expected here that the waters with levels of bromide > 100 µg/L would form brominated DBPs (Singer et al., 2002).

The level of iodine found during this survey varied between 0.9 and 16.7 µg/L (Table 5.1) and is in line with the findings of Fuge et al. (1986) who found total iodine in water sources between 0.5 and 20 µg/L. Interestingly the ratio of bromine to iodine here varied considerably between 1 and 22%, which indicates no specific trend between the level of bromine and iodine in the water sources.

### 5.3.2 DBP levels from different water sources

#### *5.3.2.1 HAAs*

The concentrations of nine HAAs from the 11 treated waters were quantified after exposure to chlorine and monochloramine (Figure 5.1). In Figure 5.1, chlorine data are represented as the treatment work reference only (e.g. B1) and the monochloramine data are shown as $NH_2Cl$-work reference (e.g. $NH_2Cl$-B1). It is clear that using monochloramine produced significantly less HAAs (average reduction of 77%) when compared to chlorine. These findings compare well with previous studies that have looked at HAA formation when using preformed monochloramine (90 to 95% reduction) (Cowman and Singer, 1996; Guay et al., 2005).

When chlorine is used as the disinfectant (Figure 5.1), considerable variation was observed between the individual waters with HAA levels ranging from 5.0 to 69 µg/L, with an average value of 37 µg/L. It is the first FP data available for HAAs in England

and Wales, although Malliarou et al. (2005), who reported their data on a regional basis, found means of 35, 52 and 95 µg/L in finished waters from three regions investigated in England and Wales. Here, no relationship could be identified between water source type and HAA levels.

Across the chlorinated water samples, the major species formed were TCAA (ranging from 1.0 to 40 µg/L) and DCAA (ranging from 2.5 to 22 µg/L). Sérodes et al. (2003) also found TCAA and DCAA to be the major species formed in treated waters from Quebec exposed to FP tests using chlorine. On a mass basis, DCAA and TCAA were followed here by BDCAA, BCAA, MCAA and DBCAA. For all waters, MBAA, DBAA and TBAA were the least concentrated, with TBAA not always detected.

The ratio of TCAA:DCAA varied across the chlorinated samples, with TCAA being predominant in six of the treated waters (B2, L2, UR1, UR2, UR3 and BR1), and DCAA for the remaining waters (B1, L1, LR, BR2 and BR3). This variation in ratio was also observed by Sérodes et al. (2003). The excess chlorine used during FP tests as well as the bromine concentration are believed to be the cause. When the bromine concentration was ≤ 75 µg/L, TCAA was predominantly formed here. When there was a high concentration of bromine (> 100 µg/L) (water samples B1, LR, BR2 and BR3) and an excess of chlorine, it is believed that bromide reacted to form hypobromous acid ($HOBr/OBr^-$), which is known to react with NOM faster than aqueous chlorine (Westerhoff et al., 2004). Consequently, the NaOCl to the NPOC ratio (NaOCl:NPOC), on a mass basis, decreased as the bromine increased. Miller and Uden (1983) amongst others found that at lower NaOCl:NPOC, the relative amount of DCAA formed was higher than that of TCAA, which was observed here. For example BR1, with a bromine concentration of 14 µg/L, formed 22 µg/L of DCAA and 40 µg/L of TCAA, whereas LR, with a bromine concentration of 209 µg/L formed 16 µg/L of DCAA and 12 µg/L of TCAA.

In addition, it was observed here that treated waters (LR, BR2 and BR3) with high levels of bromine (> 100 µg/L) formed between 43 and 52% of brominated species of the total HAA. Peters et al. (1991) found that brominated species accounted for 60% of the nine HAAs in a study of highly brominated Dutch waters (bromide concentration between 100 and 500 µg/L). Furthermore, it was observed here that in low bromine-

containing waters (≤ 75 µg/L), chlorinated HAAs dominated over brominated HAAs, as previously found by Golfinopoulos and Nikolaou (2005) and Ates et al. (2007).

Neither SUVA nor NPOC were effective surrogates for predicting the formation of HAAs in these waters. Correlations between water quality parameters and DBP-FP will be investigated in detail later in this chapter.

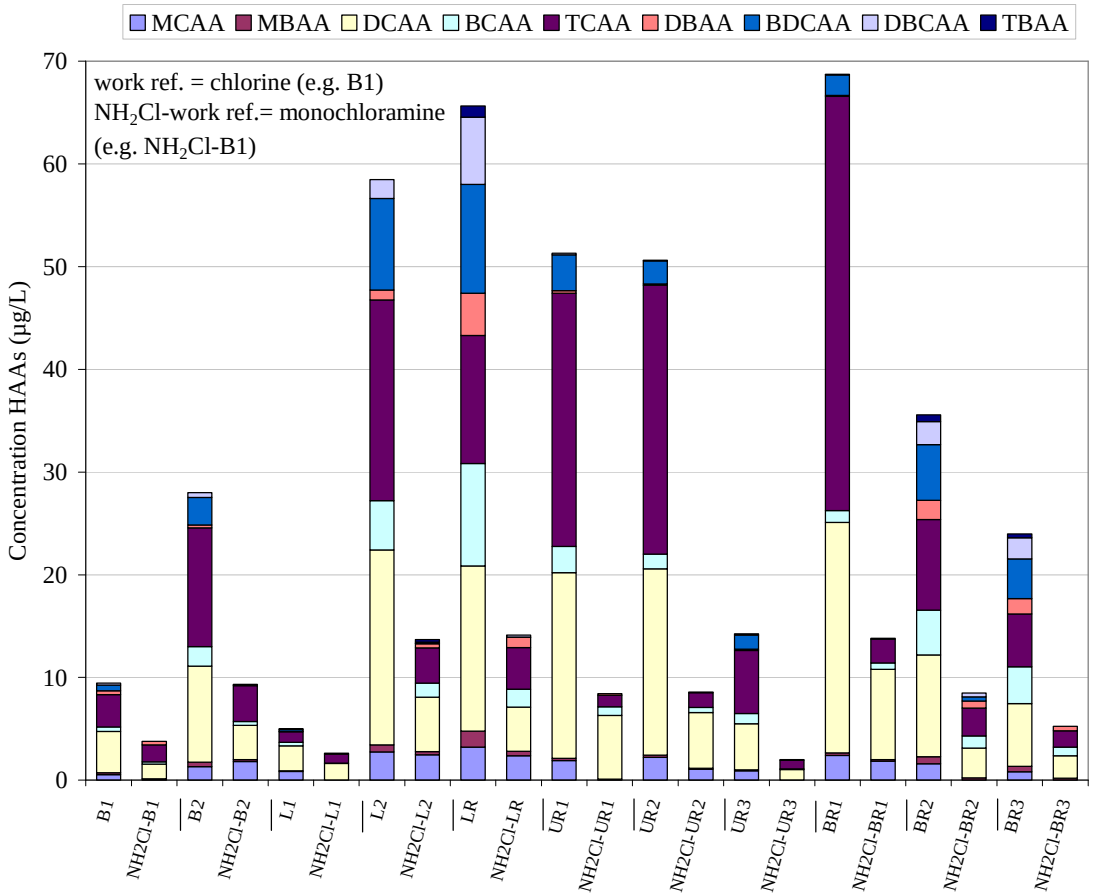



Figure 5.1 Distribution of HAAs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

When monochloramine was used as the disinfectant the highest concentration of HAAs formed was 14 µg/L (L2, LR and BR1) and the average concentration was 8.2 µg/L (Figure 5.1). DXAAs, and in particular DCAA, were observed to be the predominant HAAs formed in all the monochloramine water samples, comprising at least 60% of the total HAA formation. Karanfil et al. (2008) and Cowman and Singer (1996) both reported DXAA to be the main HAA species when using monochloramine and, in their studies, constituted 80 and 65% respectively of the total HAA formed. The

concentration of MXAA was always the lowest of the HAAs measured, but did contribute a maximum of 20% in some cases.

The difference in HAA concentrations obtained with chlorine and monochloramine is mainly believed to be due to different formation routes. When using chlorine, it was concluded that its reaction with NOM preferentially forms TCAA in low bromine-containing waters. However, the formation mechanistic with monochloramine is more complex and different models have been proposed in the literature. Karanfil et al. (2007) and Hong et al. (2007) both showed that the direct reaction between preformed monochloramine and NOM is responsible for about 80% of HAA formation and that the remaining HAA formation was attributed to the dissociation of monochloramine to chlorine. Duirk and Valentine (2006) attributed the formation of DXAA to be mostly from the reaction between NOM and chlorine in equilibrium with monochloramine. The presence of bromide in the samples complicates the chemistry of the system because bromide reacts with free chlorine and/or monochloramine to form HOBr/$OBr^-$, bromamines and bromochloramine (Valentine, 1986; Diehl et al., 2000). Here, the concentration of TXAA, and especially TCAA remains high in many of the monochloraminated samples, such as B1, L2, LR, BR2 and BR3, whilst in others, such as UR1 or UR2, the main species was DCAA, making it unclear as to which mechanism is predominant.

*Bromine incorporation*

It has been found that bromine played an important role in the formation of HAAs. Indeed it was previously concluded here that:

- Levels of bromine > 100 µg/L are responsible for the predominance of DCAA in chlorinated waters.
- High bromine-containing waters (> 100 µg/L) formed more brominated HAA species than low bromine-containing waters.
- Finally, bromine in waters exposed to monochloramine preferentially form brominated DXAAs.

To assess the extent of bromine substitution in HAA when using chlorine and monochloramine, the bromine incorporation factor (BIF) was calculated (Symons et al., 1993):

$$BIF = \frac{HAABr_9(\mu mol/L)}{HAA_9(\mu mol/L)}, \qquad \text{Equation 5.1}$$

where $HAABr_9$ is the sum of the molar concentrations of bromine incorporated in the nine HAA species and $HAA_9$ represents the sum of molar concentrations of all nine HAAs. The value BIF can range from zero to three.

Calculated BIF values were plotted against the bromine concentration (Figure 5.2).

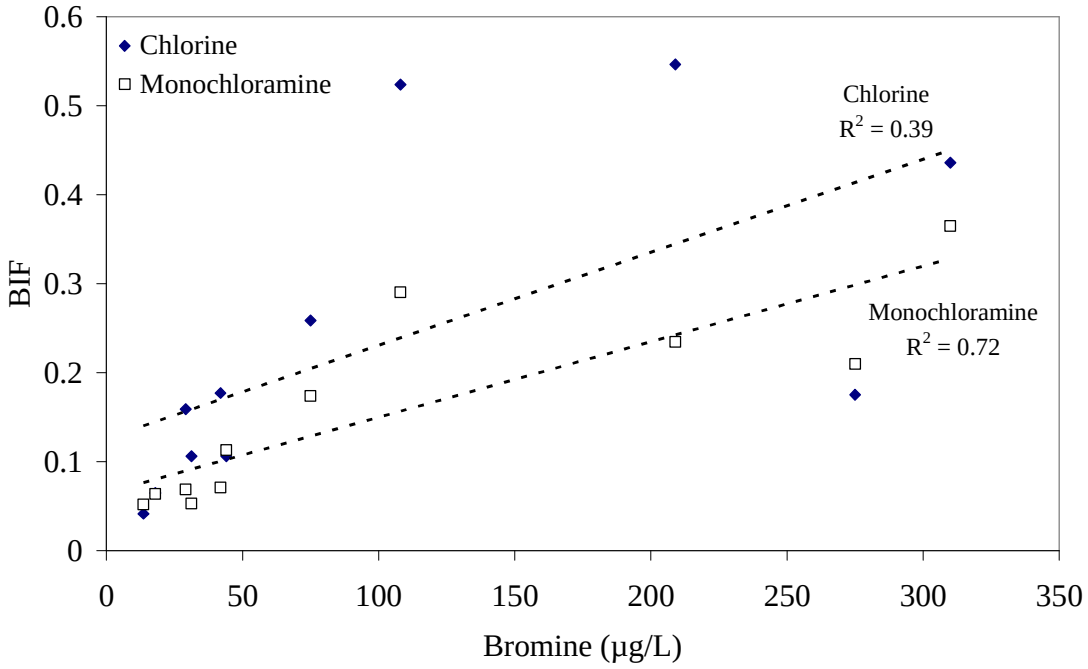



Figure 5.2 BIF in chlorinated and monochloraminated samples versus bromine concentration

The results showed limited correlations between BIF and the bromine concentration. BIF was higher in most of the chlorinated samples than in the monochloraminated samples. Chlorine is a more powerful oxidant and its reaction with bromine to form HOBr and then the formation of brominated HAAs will be faster and more predominant than with monochloramine (Deborde and Von Gunten, 2008). The correlation between BIF and bromine was better in water exposed to monochloramine ($R^2$ = 0.72) than to

chlorine ($R^2$ = 0.39). As a conclusion, the study of BIF was shown to not give conclusive evidence to justify that increasing bromide concentrations increased BIF.

#### *5.3.2.2 THMs and i-THMs*

*THMs*

The THMs formed following exposure to both chlorine and monochloramine were quantified and are presented in Figure 5.3. As with the HAAs, shifting from chlorine to monochloramine produced significantly less THMs (average reduction of 92%). It is noted that when monochloraminating, TCM could not be detected as its level was below the level of a contamination peak.

While using chlorine there was as expected considerable variation in THM levels across the 11 waters with concentrations ranging from 2.6 to 66 µg/L observed. The average concentration was 30 µg/L, which is similar to the value observed for the HAAs (average of 37 µg/L). The lowest concentration of THMs was found in L1 and the highest in LR, followed by L2. These results are similar to those for the HAAs, and specifically, the concentration of TCM was similar to that of TCAA in many samples, indicating possible common precursors. For example, in B2, TCM was 13 µg/L and TCAA was 11 µg/L, in UR1, both TCM and TCAA were concentrated at 25 µg/L and in BR1, TCM was 35 µg/L and TCAA was 40 µg/L. It was observed that L1 had a lower concentration of THMs than L2 (2.6 and 47 µg/L respectively), both waters having the same NPOC values, but L1 having a greater SUVA value than L2, which indicates that neither NPOC, nor SUVA were effective surrogate for these two treated waters.

In all the chlorinated waters with bromine < 50 µg/L, TCM was found to be the major THM species, whereas in those waters with bromine ≥ 75 µg/L brominated THMs became the major group.

When using monochloramine the concentrations of THMs were mostly below 1 µg/L, aside from B1, LR and BR2 (Figure 5.3). Interestingly, BR2, which had the highest concentration of bromine (310 µg/L) could form brominated THMs up to 13 µg/L while using monochloramine as a disinfectant. When bromine is present in the water, it reacts

with monochloramine to form bromamine species, which are highly reactive (Diehl et al., 2000). However the reactivity of bromamines with NOM to form THMs remains unknown here.

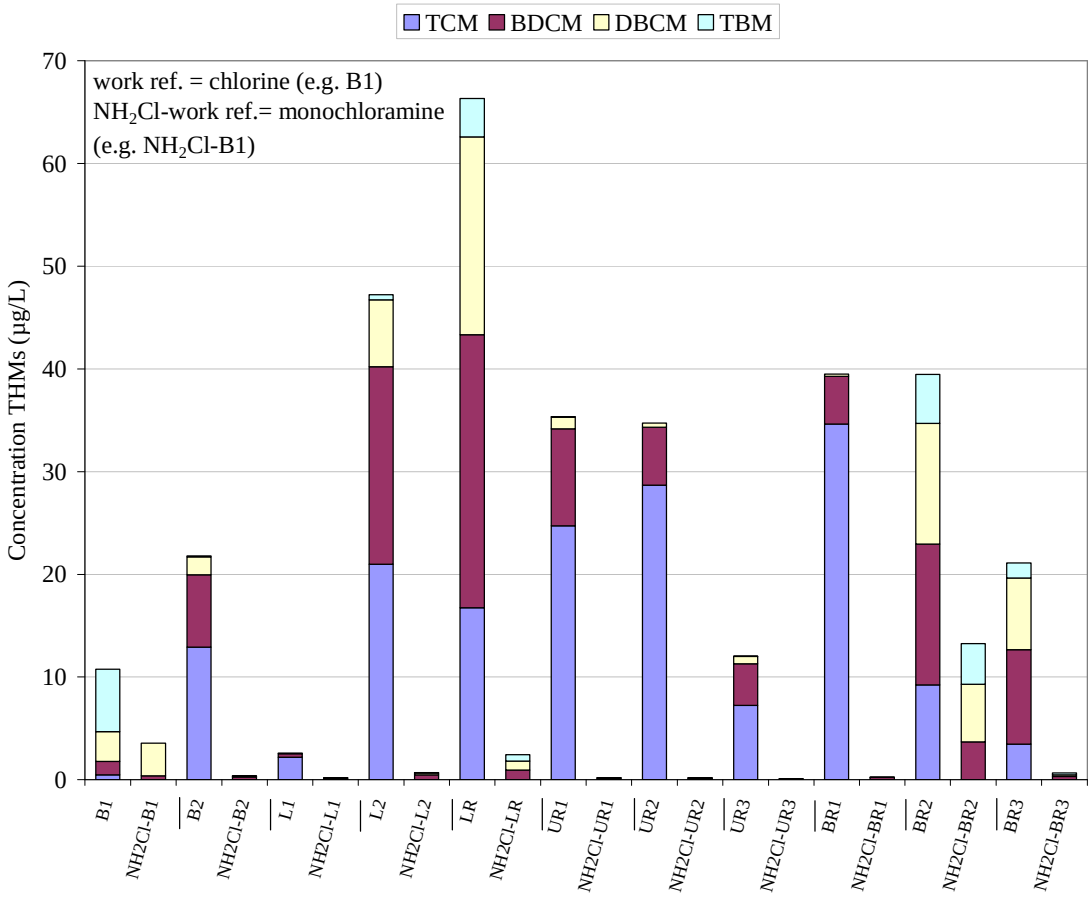



Figure 5.3 Distribution of THMs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

*i-THMs*

The concentrations of the two i-THMs formed with both chlorine and monochloramine are shown in Figure 5.4. The maximum concentration found here was 0.73 µg/L and most concentrations were below the MRL of 0.58 µg/L (see Chapter 4). Cancho et al. (2000) reported average levels lower than 1 µg/L for three species (DCIM, BCIM and DBIM) in sand filters and ozonated waters, and Krasner et al., (2006) reported a maximum of 19 µg/L for six i-THMs with DCIM and BCIM being the prevalent species. Here, it was found that the BCIM was generally at higher levels than DCIM. Overall the concentration of i-THMs formed was low when compared to THMs (Figure

5.4), with the ratio of the i-THMs to THMs being 1% on an average basis and 0.4% on a median basis. Krasner et al. (2006) reported a median ratio of 2% but for six i-THMs. It is known that chlorine oxidises iodide through to iodate ($IO_3^-$) and, hence, minimises any potential for i-THM formation (Bichsel and Von Gunten, 1999). Thus, chlorine, which is largely in excess here, generated mainly $IO_3^-$, which is believed to be the main reason for the low level of i-THMs and the fact that there is no correlation between the i-THMs and the iodine level in the water sources.

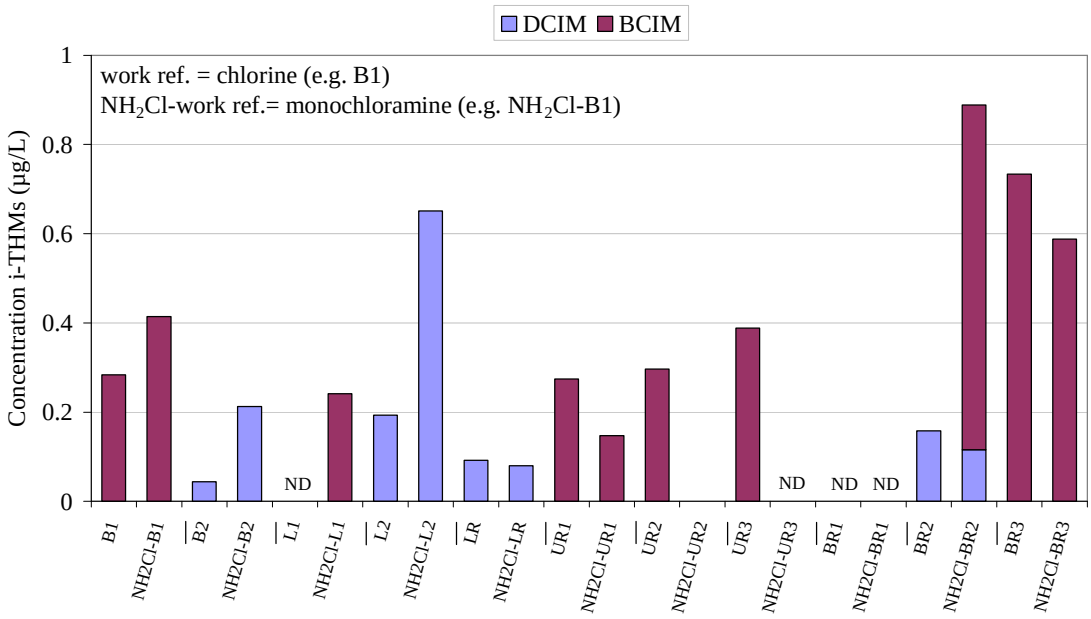



Figure 5.4 Distribution of i-THMs after 24 hours bench exposure to chlorine and monochloramine for 11 treated waters (ND – not detected)

Previous research has shown that the formation of i-THMs is favoured by monochloramine (Bichsel and von Gunten, 2000), because monochloramine, unlike chlorine, is unable to oxidise hypoiodus acid (HOI) to $IO_3^-$ meaning that HOI has a longer lifetime with monochloramine and can react with NOM to form i-THMs (Bichsel and Von Gunten, 2000a). Here, it was found that levels of i-THMs after monochloramine were between not detected to 0.89 µg/L (Figure 5.4), with five water samples (B1, B2, L1, L2 and BR2) having greater concentrations of i-THMs than after exposure to chlorine, whereas the contrary was observed in LR, UR1, UR2, UR3 and BR3. The monochloramine results presented in Figure 5.4 do not show any trend, which is most probably due to measuring close to the limit of detection. It can also be noted

that one species was detected in each sample except for BR2, where DCIM and BCIM were detected, a fact for which no explanation has been found.

As a conclusion, the use of FP tests was shown not to give conclusive evidence for the true levels of i-THMs.

#### *5.3.2.3 HANs*

The concentrations of four HANs measured in chlorinated and monochloraminated waters are presented in Figure 5.5. When using chlorine, HANs were detected in all treated waters and their concentrations were usually an order of magnitude lower than the concentrations of THMs and HAAs. Total HAN concentrations ranged between 0.023 and 5.5 µg/L, which is similar to the results of Krasner et al. (2007), who reported levels of dihalogenated HANs between approximately 0.80 µg/L and 6.2 µg/L when using FP tests for 24 hours. DCAN was the major HAN formed and contributed up to 56% of the total HAN, followed by BCAN (27%), DBAN (16%) and TCAN (2%). Dihalogenated HANs are reported to be more stable than the trihalogenated HANs by a number of studies (Coleman et al., 1984; Reckhow and Singer, 1984; Peters et al., 1990; Singer et al., 1995; Glezer et al., 1999). In addition, TCAN can undergo base-catalysed hydrolysis at pH higher 5.5 (here, the pH was 7.2) (Croué and Reckhow, 1989), which explains why it was rarely detected in the samples here.

DCAN was the most abundant species measured in chlorinated waters containing levels of bromine < 50 µg/L. In the waters with bromine ≥ 75 µg/L the brominated HANs (BCAN and DBAN) were dominant (67% total HAN). Peters et al. (1990) reported a similar value with the brominated dihalogenated HANs accounting for 60% of the total HAN in Dutch surface waters, which contained bromide concentrations ≥ 500 µg/L. It was also noticed here, that the lowland waters L1, BR2 and BR3 produced more HANs, which could be explained by the difference in precursors between lowland and upland waters remaining after treatment processes. Lowland sources are more likely to contain DON, the main precursor for HANs (Oliver, 1983; Lee et al., 2007).

Changing from chlorine to monochloramine decreased the concentration of HANs by 81% (Figure 5.5). Hua and Reckhow (2007) also found that concentrations of HAN were reduced by between 93% and 100% when using monochloramine and little dihalogenated HANs (<1 µg/L) were formed.

The speciation observed was again dependent on the presence of bromine. For example BR2, which contains 310 µg/L of bromine, formed mainly BCAN and DBAN (0.31 and 0.39 µg/L respectively), whereas UR2 with a bromine concentration of 18 µg/L formed 0.013 and 0.014 µg/L for both BCAN and DBAN, but 0.26 µg/L of DCAN. Yang et al. (2007), who studied the precursors of HAN, observed that the nitrogen precursors of DCAN are from monochloramine and nitrogen-containing compounds in the sample. The study worked with isotoped monochloramine ($^{15}NH_2Cl$) and found that the percentage of DCA$^{15}$N in the total DCAN yields varied from 8% to 78% in monochloraminated model compound solutions.

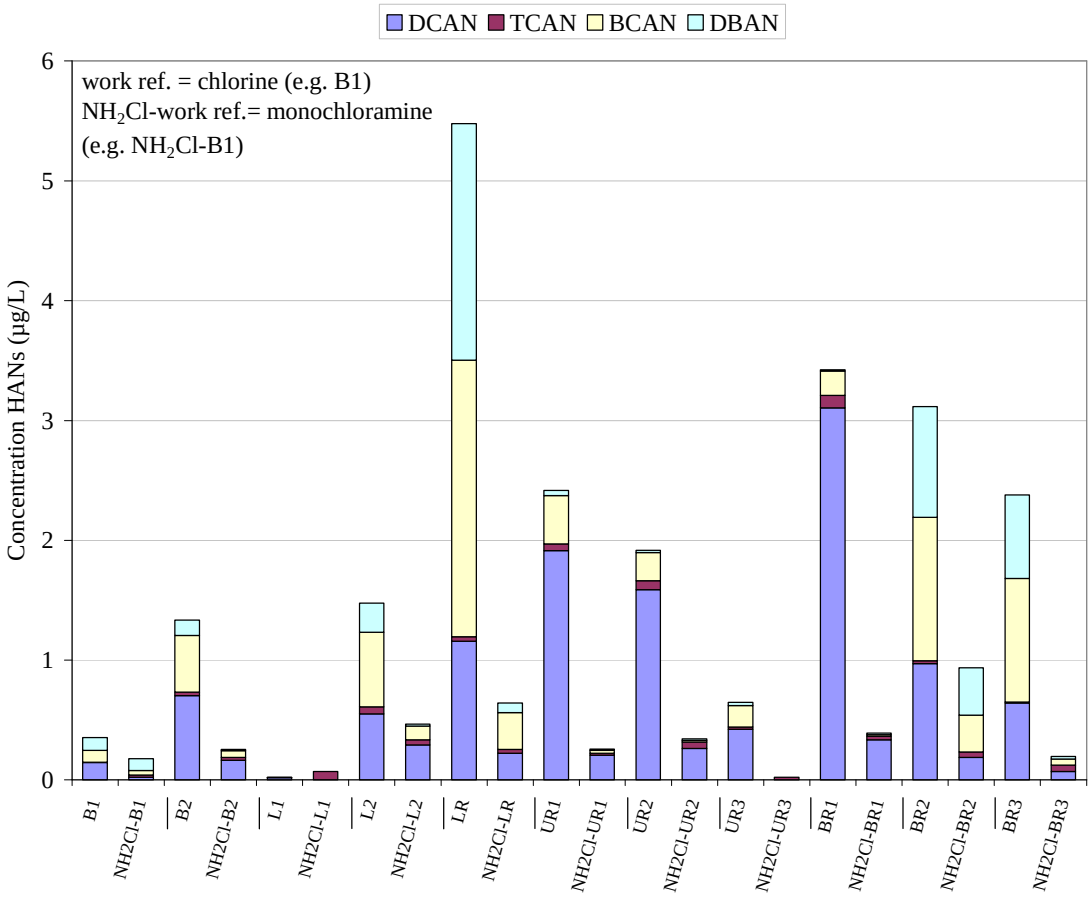



Figure 5.5 Distribution of HANs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

### *5.3.2.4 HKs, HAs and HNMs*

*HKs*

The concentrations of the two HKs formed following exposure to chlorine and monochloramine are presented in Figure 5.6. HKs were detected in all the treated waters exposed to chlorine (Figure 5.6), with concentrations ranging from 0.37 to 3.9 µg/L, with a mean value of 1.8 µg/L. The highest concentration was observed in BR1, whereas the lowest concentration was measured in L1 and B1.

1,1,1-TCP was the major HK formed in B2, L2, LR, UR1, UR2, UR3, BR1, BR2 and BR3. The greater formation of 1,1,1-TCP in the samples is believed to be the result of the excess chlorine used in FP test, involving the oxidation of 1,1-DCP to 1,1,1-TCP (Gurol et al., 1983).

The use of monochloramine resulted in an average decrease of 70% in the total HK compared to the use of chlorine (Figure 5.6); no 1,1,1-TCP was detected, which agrees with Yang et al. (2007). Monochloramine does not provide enough free chlorine to lead further substitution into 1,1-DCP, and Yang et al. (2007) found 1,1-DCP to be stable with monochloramine, which explains its abundance here (average of 32% more than with chlorine).

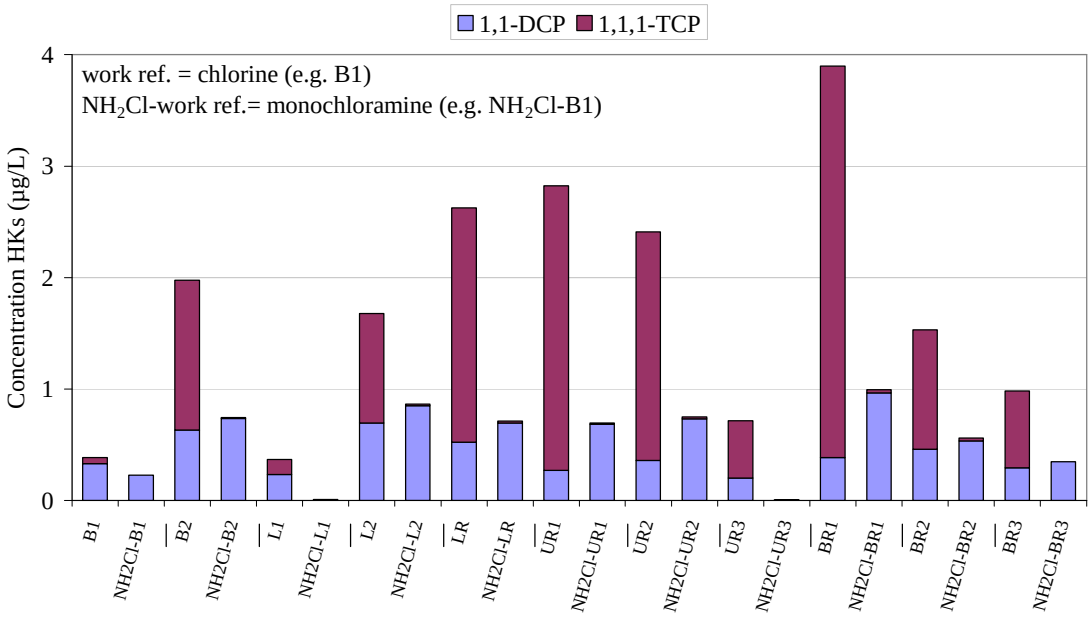



Figure 5.6 Distribution of HKs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

*HAs*

The concentration of HAs following the use of chlorine or monochloramine is shown in Figure 5.7. HAs were present in all samples after 24 hours contact time with chlorine. The minimum value was 0.92 µg/L for L1 and the maximum value was 9.5 µg/L for BR1. The average of HAs formed was 4.4 µg/L, hence this group of DBPs represented the third major class of halogenated DBPs formed (on a weight basis) after HAAs and THMs, which is in agreement with Krasner et al. (2001). The major HA detected was TCA (also called chloral hydrate). Williams et al. (1997) also found TCA to be the most prevalent DBP after HAAs and THMs and Koudjonou et al. (2008) reported TCA in drinking water made up 60% of the total HA. It has been shown previously that ozonation can increase the levels of DCA and TCA (Weinberg et al., 1993). Here, the two boreholes B1 and B2 had different concentrations of HKs, with B2, the pre-ozonated site, having a greater formation potential for DCA (0.62 µg/L) and TCA (2.4 µg/L) than B1 (0.31 and 0.61 µg/L respectively), which has no ozone.

The use of monochloramine resulted on average in a 90% decrease in the total HA concentration (Figure 5.7) and as observed by Young et al. (1995), monochloramine preferentially minimised TCA formation. Here, TCA was reduced by 92% compared to 62% for DCA.

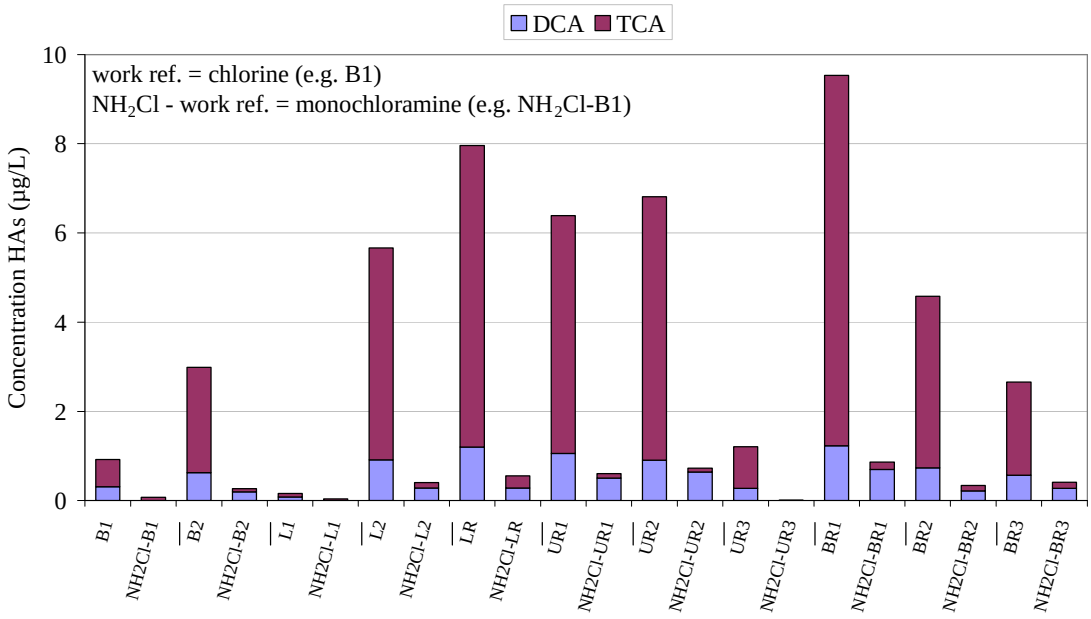



Figure 5.7 Distribution of HAs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

*HNMs*

The final group of DBPs reported here are the HNMs (Figure 5.8). The total concentration of HNMs measured after exposure to chlorine ranged from not detected to 3.4 µg/L (Figure 5.8). The predominant HNM was TCNM, with a concentration of up to 3.4 µg/L. This result was in line with Krasner et al. (2001) who reported TCNM concentrations of up to 2.0 µg/L. DBNM was detected here in B1, B2, L2, LR, BR2 and BR3, with the highest concentration found in BR2. Although other researchers have shown that pre-ozonation can increase the formation of TCNM (Hoigné and Bader, 1988) or other HNMs (Richardson et al., 1999; Plewa et al., 2004), it was not possible to see this trend here. The highest concentration of HNMs was observed in BR1, a lowland river, followed by UR1, which is an upland reservoir. Hence, the nitrogenous precursors available for the formation of TCNM are independent of the source type (e.g. lowland, upland).

On average the concentration of HNM was reduced by 81% when using monochloramine (Figure 5.8). Recently Hua and Reckhow (2007) found that when using monochloramine only traces concentrations of TCNM were found and Zhang et al. (2000) reported a decrease of 58% with monochloramine in comparison to chlorine.

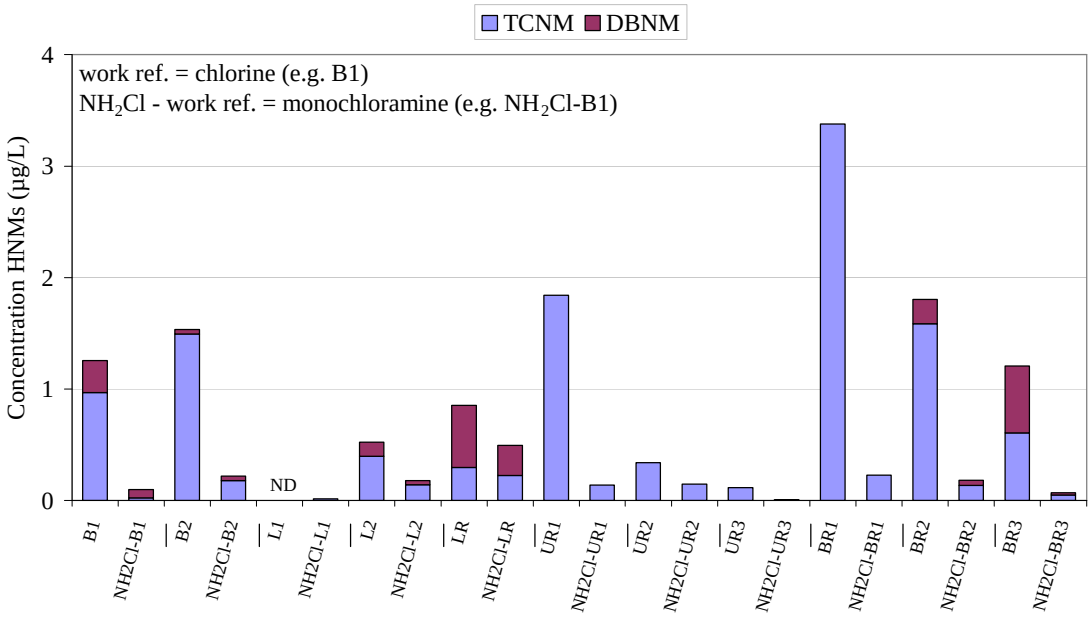



Figure 5.8 Distribution of HNMs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters (ND – not detected)

### 5.3.3 Relationships between HAAs, THMs and other DBPs

Establishing a number of relationships between DBPs would allow a better understanding of DBP formation and the main interest is to determine whether some species can be used as a surrogate for others. Here the correlation between HAAs and THMs was investigated (Figure 5.9) and it was found that for the tested waters THMs were generally a good surrogate for HAAs when chlorine was used (coefficient of correlation $R^2 = 0.82$). The slope of this correlation was 1.21, which suggests that there is slightly more than one µg of HAA formed for one µg of THM. No correlation could be found between THM and HAAs when using monochloramine. The good correlation between THMs and HAAs is useful for quality control and monitoring in water utilities because, in general, laboratory analyses for HAAs cost considerably more and are also more time consuming than the THM analyses (Sérodes et al., 2003). Nevertheless, this correlation has its limitations. For example, a strong relationship ($R^2 = 0.92$) has been observed by Ates et al. (2007) while using FP tests, as well as Nissinen et al. (2002) ($R^2 = 0.90$) in their final waters, whereas Sérodes et al., 2003 found moderate relationships ($R^2 = 0.56$, 0.57 and 0.63) with FP tests. Malliarou et al. (2005) reported a good relationship between THMs and HAAs in final waters from two geographically different regions ($R^2 = 0.82$ and 0.90), whereas they found a poor correlation in the waters of their third region investigated and suggested that total THM could not be assumed to be a good indicator for HAA levels. The results here proved that THMs can be a surrogate for HAAs, but with uniform conditions of experiments used in FP tests.

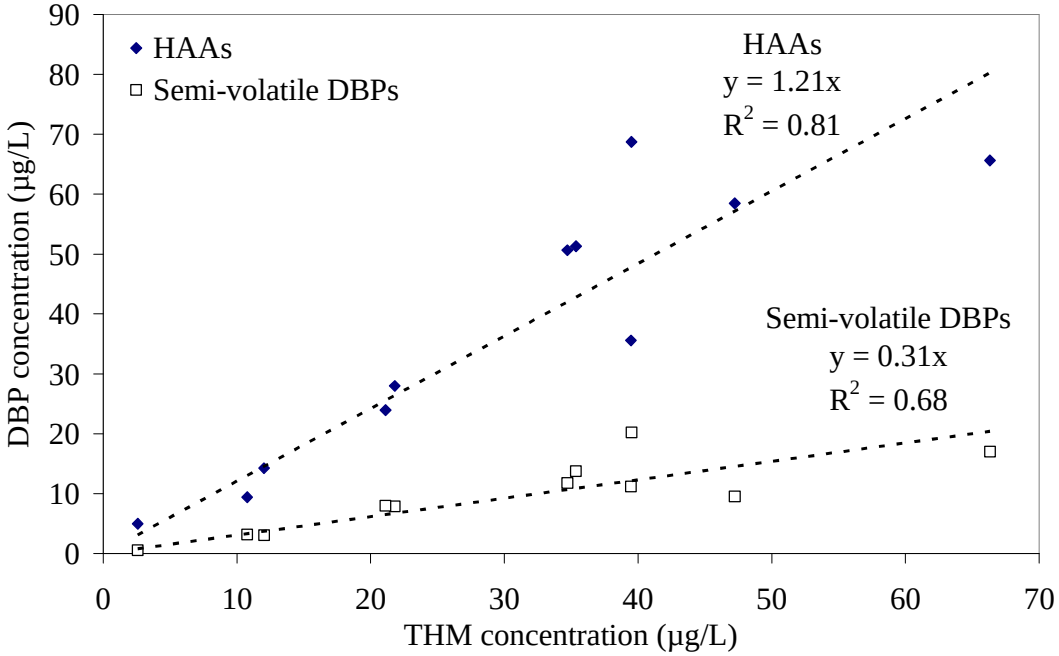



Figure 5.9 Correlation between THMs with HAAs and the semi-volatile DBPs (chlorine FP tests)

This study is the first to report levels of DBPs other than just THMs and HAAs in UK treated waters and therefore, concerns have been expressed about the practicality of performing several DBP analyses and processing in water utility's routine monitoring. Previously it was shown that THMs could be used as a surrogate to determine the level of HAAs under the uniform conditions used here. Moderate relationship was also found between the total THM and the sum of the semi-volatile DBPs (HAN, HA, HK, i-THM and HNM) measured after exposure to chlorine (Figure 5.9). The $R^2$ obtained for the collated semi-volatile DBPs was 0.68, which is in line with a previous correlation ($R^2$ = 0.76) found between total THM and non-THM DBPs in drinking waters (Krasner et al., 1989). This correlation suggests that the control of THM precursors is closely linked to the control of other DBP precursors. As explained by Krasner et al. (1989) this trend is valid for the sum of the measured halogenated DBPs but it does not give similar trends for individual compounds; e.g. comparing total THMs to HNMs yields an $R^2$ of only 0.08. In terms of regulation, it is interesting to note that the regulatory limit of 100 µg/L for the $THM_4$ would fail a regulation of 80 µg/L for the nine HAAs, currently under consideration by the European Union (Cortvriend, 2008). Indeed from the correlation

found here, if 100 µg/L of $THM_4$ would be formed, it would be expected 121 µg/L of $HAA_9$. To achieve a concentration of 80 µg/L for $HAA_9$, $THM_4$ should be concentrated to about 65 µg/L.

Overall observations showed better correlations between species while using chlorine than during monochloramine. No further investigation was undertaken.

### 5.3.4 Relationships between NPOC, UV and SUVA with DBPs

Relationships between NPOC, UV and SUVA with HAAs, THMs and the semi-volatile DBPs were investigated with chlorine FP test data. NPOC, UV and SUVA have been used previously as surrogates for measuring DBPs as they are easier, cheaper and faster to measure than DBPs (Goslan et al., 2002; Parsons et al., 2005; Ates et al., 2007). Firstly, HAAs, THMs and semi-volatile DBPs have been plotted against NPOC (Figure 5.10) and correlation ($R^2$ values) between NPOC and HAAs, THMs and the semi-volatile DBPs (collated together) were moderate (0.51, 0.63 and 0.56 respectively). Although stronger correlations have been reported, such as White et al. (2003), who found an $R^2$ of 0.86 and 0.87 for HAAs and THMs respectively to NPOC, it is likely that correlations observed in a single sample are better than correlations observed from a range of water sources (Reckhow and Singer, 1990). It must also be considered, that a number of other parameters, such as the bromide, iodine as well as the interactions between parameters can affect the formation of DBPs, and therefore, the results, here, are limited to a single analysis. In terms of semi-volatile DBPs as separate species it was observed that NPOC correlated well with HANs ($R^2$ = 0.82) and moderately with HAs ($R^2$ = 0.52) (Table 5.2). However, no correlations were found between NPOC with i-THMs, HNMs and HKs.

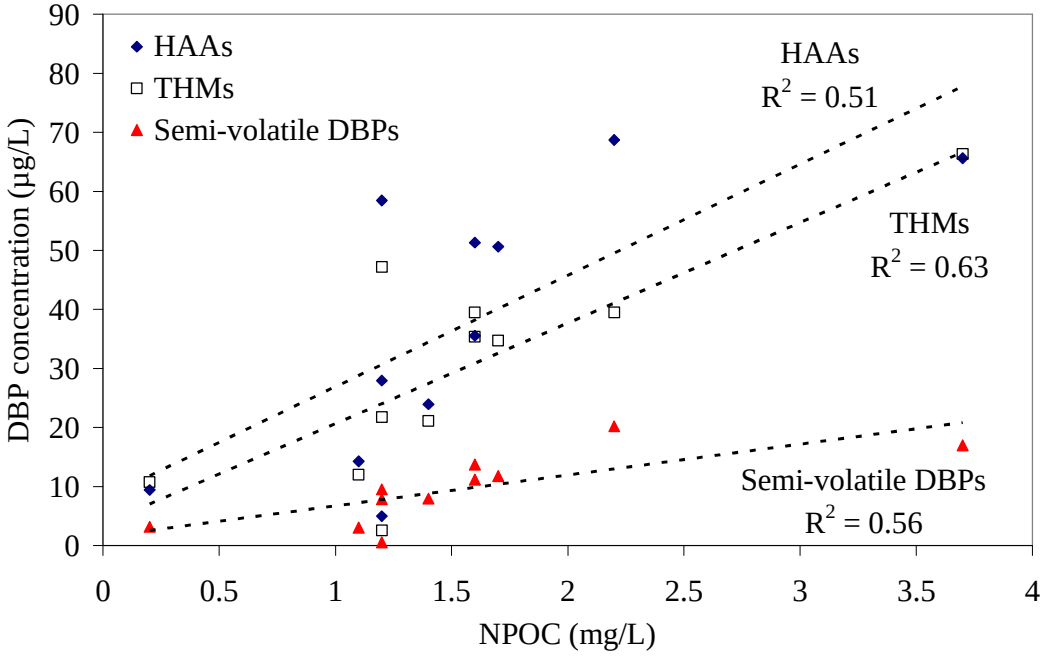



Figure 5.10 Relationship between NPOC and DBPs

No correlations were found between either $SUVA_{254}$ or $UV_{254}$ and DBPs (Table 5.2). For example an $R^2$ of 0.11 was found between $UV_{254}$ and HAAs, an $R^2$ of 0.06 between $UV_{254}$ and THMs and an $R^2$ of -0.07 between $UV_{254}$ and the collated semi-volatile DBPs. Individual groups of semi-volatile DBPs did not show any correlation with $UV_{254}$ (Table 5.2). Further correlations were investigated by considering the coagulated waters only in relationships to DBPs. The best $R^2$ was obtained between $UV_{254}$ with the semi-volatile DBPs (adding together) ($R^2$ = 0.82), followed by with the HAAs ($R^2$ = 0.78) and with the THMs ($R^2$ = 0.49) (Figure 5.11). The investigation of the individual groups of semi-volatile DBPs showed good relationships between $UV_{254}$ with HKs ($R^2$ = 0.72) and HAs ($R^2$ = 0.86) and moderate correlations with i-THMs ($R^2$ = 0.50), but no correlations existed between $UV_{254}$ with HNMs and HANs (Table 5.2).

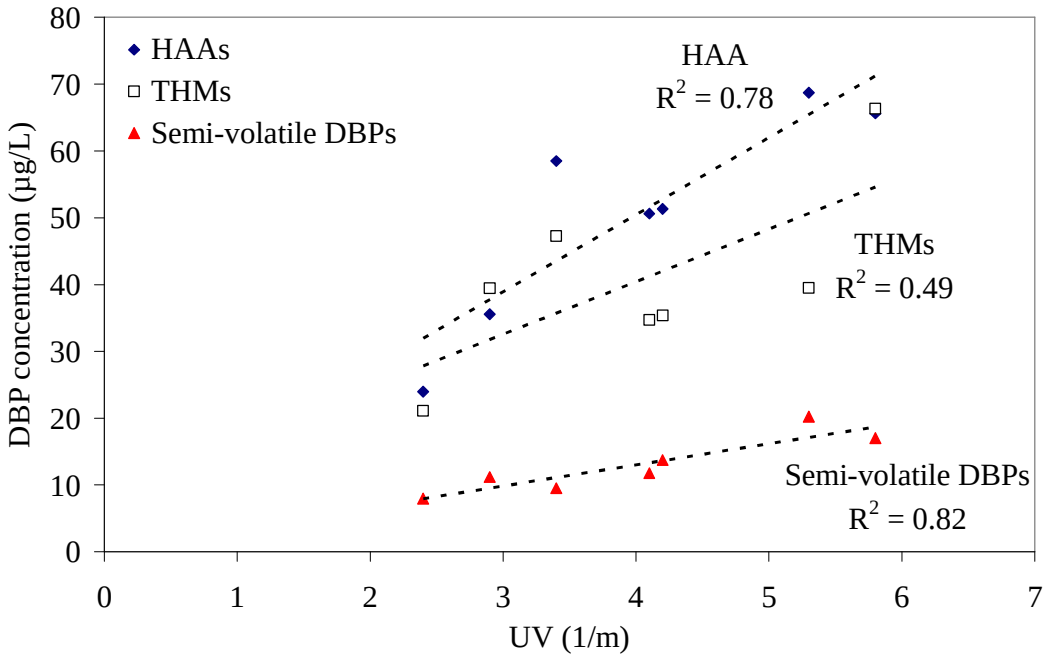



Figure 5.11 Relationship between $UV_{254}$ and DBPs for coagulated waters

Finally, the correlation between $SUVA_{254}$ with DBPs was non-existent when all the data were considered. Data presented in Table 5.2 show $R^2$ between 0.003 and 0.27 for every group of DBPs individually. Investigation of the coagulated waters only did not show any improvements and it was therefore concluded that the waters investigated here did not present any correlation with SUVA.

Table 5.2 Correlation between DBPs and water characteristics

| DBPs (µg/L) | Coefficient of correlation ($R^2$) | | | |
|---|---|---|---|---|
| | NPOC (mg/L) | UV (1/m) | | SUVA (L/m-mg C) |
| | | All data | Coagulated waters | |
| HAAs | 0.51 | 0.11 | 0.78 | 0.15 |
| THMs | 0.63 | 0.06 | 0.49 | 0.23 |
| i-THMs | 0.07 | 0.09 | 0.50 | 0.003 |
| HANs | 0.82 | 0.09 | 0.45 | 0.27 |
| HKs | 0.42 | 0.11 | 0.72 | 0.12 |
| HAs | 0.52 | 0.11 | 0.86 | 0.16 |
| HNMs | 0.03 | 0.03 | 0.06 | 0.25 |

Overall, the results showed a lot of variations in correlations between DBPs and the water characteristics. Investigation of coagulated waters only showed improved

correlations between $UV_{254}$ and some of the DBPs, but this was not the case for NPOC and SUVA and their correlations to DBPs. This presented work showed that in general water characteristics could not be considered as surrogate for the measurement of DBPs when a range of English and Welsh treated waters were collated together. Therefore, more work is needed to investigate several samples throughout the year from one source to determine if correlations between water characteristics and DBP formation could be specific to individual sources as expressed by Reckhow and Singer (1990). In addition, the results obtained here, were based on a single correlation analysis and therefore, the results are limited.

## 5.4 CHAPTER SUMMARY

This study was designed to determine the formation potential of HAAs, THMs and semi-volatile DBPs formed from a range of treated waters after exposure to chlorine or monochloramine. General results are summarised in Table 5.3. The main results were:

- Variable levels of HAAs, THMs and semi-volatile DBPs were formed.
- Levels of TCM were similar to the levels of TCAA.
- The prevalent classes of DBPs were HAAs and THMs; HAs were found to be the third major group.
- The impact of bromide on the formation of DBPs is well documented in the literature and herein the data reaffirmed that more bromide species are formed in high bromide-containing waters. For HAAs, brominated species are predominant when bromine was > 100 µg/L, whereas the brominated THMs dominated when bromine was ≥ 75 µg/L.
- The use of FP test was found unsuitable for the quantification of i-THMs.
- A general decrease in all the investigated species has been observed when shifting from chlorine to monochloramine with the one exception being 1,1-DCP.
- Under the controlled conditions used here, THMs correlated well with HAAs, and the semi-volatile DBPs collated together.

- The combination of good, moderate and non-existent correlations between water characteristic parameters and DBP-FP were mainly attributed to the fact that several water sources were studied, giving a complex matrix in which correlations were not always achievable.

Table 5.3 Summary of the findings

| DBPs | DBP levels (µg/L) | | Shifting $Cl_2$ to $NH_2Cl$ | Impact of geographical location | Relationships |
|---|---|---|---|---|---|
| | $Cl_2$[a] | Preformed $NH_2Cl$[b] | | | |
| HAAs | 5.0 – 68 | 2.1 – 14 | Overall decrease DXAA>TXAA | Variable between sources | THMs and NPOC |
| THMs | 2.6 – 66 | 0.1 – 13 | Overall decrease | Variable between sources | HAAs, SV[e]-DBPs and NPOC |
| i-THMs | ND[c] – 0.73 | ND[c] – 0.89 | NC[d] | NC[d] | None |
| HANs | 0.02 – 5.5 | 0.02 – 0.94 | Overall decrease | Highest in lowland sources | THMs and NPOC |
| HKs | 0.37 – 3.9 | 0.01 – 1.0 | 1,1-DCP increase 1,1,1-TCP decrease | Variable between sources | None |
| HAs | 0.92 – 9.5 | 0.01 – 0.86 | DCA slight decrease TCA great decrease | Variable between sources | THMs and NPOC |
| HNMs | 0.003 – 3.4 | 0.05 – 0.5 | Overall decrease | Variable between sources | None |

[a] Chlorine; [b] Monochloramine; [c] Not detected; [d] Not conclusive; [e] Semi-volatile.

# Chapter 6

# UNDERSTANDING AND CONTROL OF HAA AND THM FORMATION IN TREATED WATERS

## 6.1 INTRODUCTION

NOM is described as an intricate mixture of organic compounds that occurs universally in ground and surface waters. Whilst NOM itself is not problematic, it can be converted into DBPs when in contact with disinfectants used during water treatment (Krasner et al., 1989). In the UK, it has previously been shown (Chapter 5) that treated water has the potential to form HAAs and THMs under specific controlled conditions. Nevertheless, many factors influence the formation of HAAs and THMs. These factors include the pH, the water temperature, the contact time with the disinfectant and the disinfectant type (Liang and Singer, 2003). Furthermore, the type and concentration of NOM as well as the concentration of bromide have a direct impact on the levels of THMs and HAAs formed (Cowman and Singer, 1996; Hua and Reckhow, 2007).

It is known that the formation of THMs is enhanced at high pH (Carlson and Hardy, 1998), however, the effect of pH on the formation of HAAs is equivocal. Overall, HAA formation increases with decreasing pH (Krasner, 1999). It is well established that the DXAA concentration remains constant, while the TXAA concentration decreases with increasing pH (Singer et al., 2002). The impact of bromide on the formation of DBPs is well documented in the literature and the conclusions of Chapter 5 reaffirmed that more bromide species are formed in high bromide-containing waters. In Chapter 5, it was also found that for HAAs, brominated species are predominant when bromine was > 100 µg/L, whereas the brominated THMs dominated when bromine was ≥ 75 µg/L. The experiments in Chapter 5 were undertaken after 24 hours contact time with the disinfectant. Contact time is an important parameter and it is well known that while using chlorine, DBP formation increases with increasing contact time and chlorine dose applied (Fleischacker and Randtke, 1983). High NOM concentrations have generally been associated with high DBP concentrations (Liang and Singer, 2003; Fearing et al., 2004; Sharp et al., 2006). In the UK, chlorination tends to occur after the water has been

treated by a coagulant and filtered (Parsons, 2006), which is different from US treatment practices where pre-chlorination is widely used (Singer et al., 2002). After conventional treatment processes, NOM is mainly hydrophilic in character and low in concentration (Goslan et al., 2002). However, hydrophilic NOM has been reported to contribute substantially to the formation of DBPs especially for waters with a low humic (hydrophobic) content (Hua and Reckhow, 2007). Specifically, Hwang et al. (2001) reported the hydrophilic acid + neutral fraction is the most reactive towards the formation of THMs and HAAs, entailing the water companies to focus on the removal of this part of NOM to have a better control of DBPs.

Water utilities are also looking towards alternative disinfectants to meet the regulations stipulated previously in this thesis. In this direction, chloramines have been identified as an effective alternative disinfectant because they generally result in lower concentrations of THMs and HAAs (Speitel, 1999; Diehl et al., 2000). In Chapter 5, HAAs and THMs have been found to decrease when shifting from chlorine to monochloramine. With concurrent addition of chlorine and ammonia, the HAA formation is typically 5 to 20% of that observed with chlorine alone (Speitel, 1999) and DXAAs are the most commonly formed DBPs comprising > 90% of the total HAA (Diehl et al., 2000).

Controlling DBPs requires extensive experimental procedures and chromatographic analysis, which is time and cost consuming. Therefore, many models have been developed to predict THM and HAA formation (Amy et al., 1987; Adin et al., 1991; Chowdhury et al. 1991; Garcia-Villanova et al., 1997; Clark, 1998; Rodriguez et al., 2000; Gang et al., 2003). However, the creation of predictive models requires a large database of exiting results and sometimes tends to over- or under-predict DBPs (Greiner et al., 1992). One model that shows good fitting to experimental data is the mathematical chlorine decay model based on parallel first order reaction, detailed by Gang et al. (2002). By integration of this model, it is possible to accurately predict HAAs and THMs under specific experimental conditions.

The aims of this chapter were to (1) investigate the impacts of pH, temperature, bromide concentration, contact time with chlorine and the use of alternative disinfectant on the controlled formation of HAAs and THMs from two distinctly different waters; (2) to

determine the principal fractions responsible for the formation of HAAs from these two waters and finally (3) to fit the chlorine decay data to the model proposed by Gang et al. (2002) and to propose a model for the prediction of HAAs and THMs. The waters were chosen from different geographical regions in the UK and collected after treatment, but before disinfection. They have been primarily examined in the survey described in Chapter 5, and showed potential to form HAAs and THMs. This work is specific to THMs and HAAs, because THMs are regulated in the UK and HAAs are considered for regulation (Cortvriend, 2008). The first and the third aim were undertaken with five HAAs (MBAA, DCAA, TCAA, BCAA and DBAA), because of the standard commercially available at the time of this study. Thereafter, $HAA_9$ became available and were hence used for the second part of this chapter. This work examines the sensitivity of DBP formation to differences in water character and establishes whether treated UK waters follow the trends identified for untreated US waters regarding THM and HAA formation.

## 6.2 MATERIALS AND METHODS

### 6.2.1 Water sample and characterisation

All experiments were undertaken with samples collected in Spring 2006 from two water utilities: Anglian Water from East Anglia (lowland water) and Yorkshire Water (upland water). The WTWs were selected because of their different NOM content as well as their different geographical locations. The lowland water reservoir is situated in the East Anglian region of England in the South East. The reservoir is on a plateau with nearly all of its water being extracted from a local river. The upland water reservoir is situated in northern England. It is fed from a range of reservoirs set in peat-rich moorlands. A basic description of the lowland and upland water treatments are shown in Figure 6.1 and Figure 6.2. The sampling point at each work is denoted by a *. Both samples did not contact with any disinfectant.

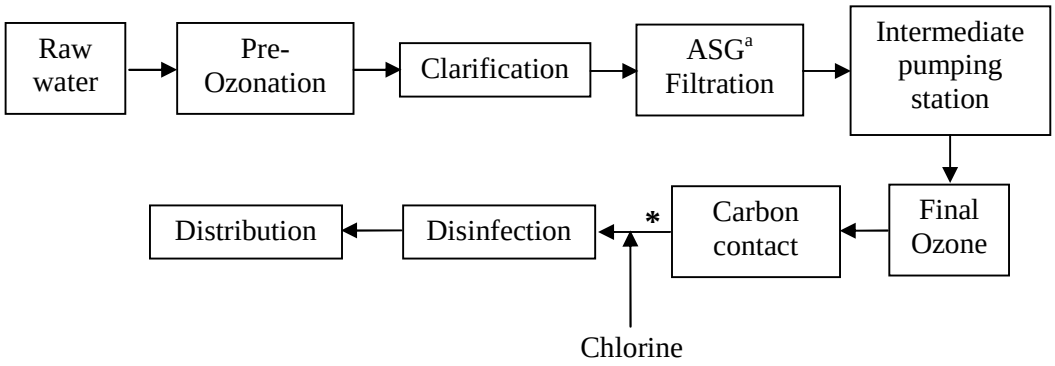



Figure 6.1 Process schematic of the lowland WTW ([a] Anthracite, sand and garnet)

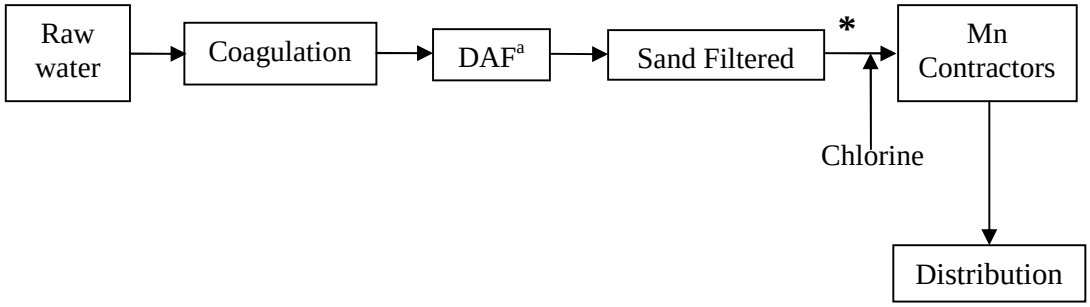



Figure 6.2 Process schematic of the upland WTW ([a] Dissolved air flotation)

A large volume of each water was collected (≥100 L) and stored in the fridge at 7ºC until used. Periodic measurements of pH, NPOC, $UV_{254}$ and bromide concentration were carried out and results were consistent indicating the stability of NOM. NPOC, $UV_{254}$, and pH analytical measurements are as described in Chapter 5, Section 5.2.

#### *6.2.1.1 Measurement of bromide using IC*

Analysis of bromide was carried out with an IC system, (Dionex, DX500 series, UK). This consisted of an IonPac AG9HC guard column (4 x 50 mm), an IonPac AS9HC separation column (4 x 250 mm), an anion electrolytic suppressor (Atlas, 4 mm, UK) in auto-suppression recycle mode, an SC 20 suppressor controller, an ED 40 in conductivity mode and a 250 µL sample loop (all supplied by Dionex, UK). Instrumental control and data collection were performed using PeakNet 5.11 chromatography workstation (Dionex, UK). All the tubing in the chromatography path (from pump outlet to exit of cell) was PEEK (0.125 mm ID). The eluent was 9 mM

sodium carbonate ($Na_2CO_3$) anhydrous (Fisher Scientific, UK). The suppressor current was set to 72 mA and the eluent flow rate was kept at 1.0 ml/min. A calibration curve was made with standards of bromide at 10, 25, 50, 75, 100 and 200 µg/L.

#### *6.2.1.2 Alkalinity*

Alkalinity is the acid neutralising capacity of the water. It can be determined by titration. Alkalinity depends on the end point used in the titration. For routine analysis, an end point of pH 4.5 is used. Titration was made with 0.02 M hydrogen chloride (HCl). Bromocresol green/methyl red indicator was prepared as specified in the Standard Method 2320B (APHA, 1998).

A sufficiently large sample to provide a good volumetric precision but small enough to give a good end point was used. The standard method recommends a volume titrant of about 20 mL. The volume of sample was thus placed in a conical flask. Pure water was added to make-up the volume to approximately 100 mL. Two to three drops of bromocresol green/methyl red indicator were then added to the volume of sample. Then the titration was carried out with 0.02 M hydrogen chloride until the end point was reached (using the bromocresol green/methyl red indicator gives a colour change from blue to pale yellow). Then the alkalinity is calculated using the following equation:

$$\text{Alkalinity, mg } CaCO_3/L = \frac{At \times N \times 50{,}000}{\text{mL sample}} \qquad \text{Equation 6.1}$$

where At = mL standard acid titrant and N = normality of standard acid used.

### 6.2.2 Fractionation

To determine the hydrophilic/hydrophobic NOM ratio, 50 litres of the treated waters were fractionated by XAD and cation exchange resin adsorption techniques into their hydrophobic neutral, hydrophobic acid, transphilic, hydrophilic base and hydrophilic acid + neutral fractions. The method used was adapted from Leenheer et al. (2004). The column capacity factor (k') was 60 for both samples (Goslan, 2003). The recovery of NOM was 90 and 113% for the lowland and upland water respectively.

The resins used were Amberlite XAD-7HP resin and Amberlite XAD-4 resin (Rohm & Haas, Germany). Amberlite XAD-7HP is an acrylic ester polymer and is equivalent to XAD-8; Amberlite XAD-4 is a styrene DVB polymer. Amberlite 200 strongly acidic cation exchanger has a sulfonated polystyrene/DVB matrix (Sigma-Aldrich, UK). The XAD resins were precleaned by sequentially Soxhlet extracting for 48 hours each with methanol, acetonitrile and methanol again to remove impurities. Before use the resins were packed into columns and rinsed with pure water until the column effluent NPOC was < 2 mg/L (Malcolm and MacCarthy, 1992).

The fractionation procedure is presented below in Figure 6.3.

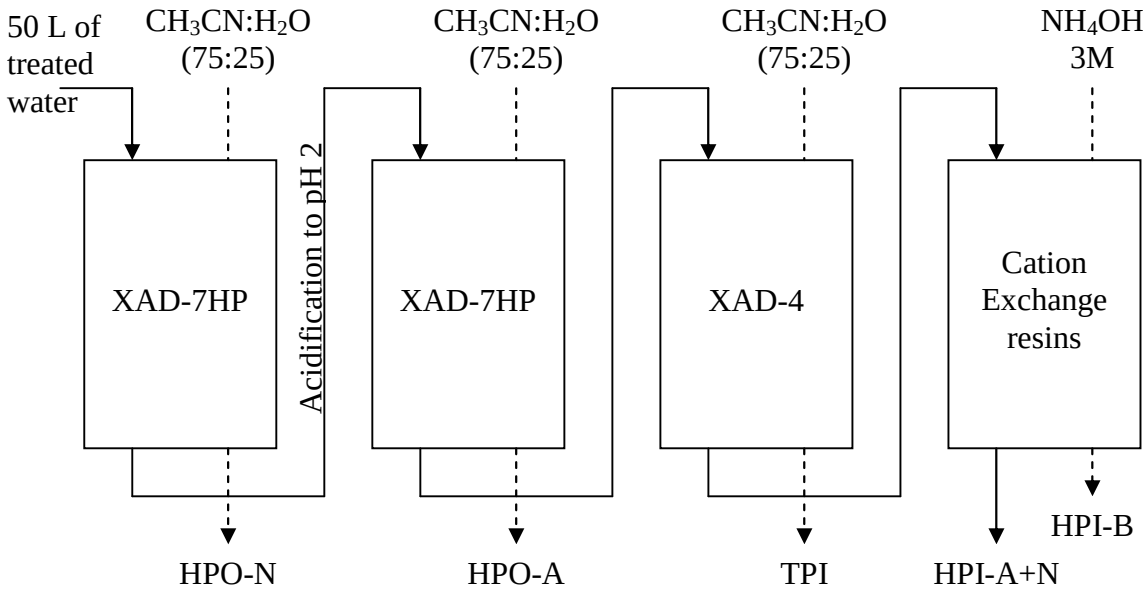



Figure 6.3 Schematic of the fractionation procedure

Fifty litres of lowland water was passed through XAD-7HP resin. The column was back eluted with 400 mL of a solution of acetonitrile ($CH_3CN:H_2O$ (75:25)). The hydrophobic neutral (HPO-N) was desorbed from the resin. The effluent collected was acidified to pH 2 and again put through the XAD-7HP column. Then the column was back eluted with 400 mL of the same solution ($CH_3CN:H_2O$ (75:25)). The hydrophobic acid (HPO-A) was desorbed from the resin. The eluate was put through the XAD-4 and the transphilic fraction (TPI) was desorbed by back eluting the resin with again 400 mL

of $CH_3CN$:$H_2O$ (75:25). Finally the effluent was passed through the cation exchange resin. The overall effluent was the hydrophilic acid + neutral fraction (HPI-A+N), whereas the desorbed fraction (with 3M of ammonium hydroxide ($NH_4OH$)) was the hydrophilic base fraction (HPI-B).

After cleaning the XAD resins with pure water and regenerating the cation exchange resins (using three to six bed volume of 1 to 10% of acid sulphuric as a regenerant, with a flow between 1 to 10 m/h), 50 litres of the upland water was fractionated using the same procedure.

### 6.2.3 DBP-FP

#### *6.2.3.1 Sample preparation for the determination of parameter impacts and the modelling study*

Preparation of the solutions and details of the suppliers are given in Chapter 5, Section 5.2.3. Here, samples were chlorinated at pH 6, 7 and 8 at room temperature (20ºC) to determine their DBP-FP. Phosphate buffer was used to adjust the pH. In addition one set of samples for each water was chlorinated at pH 7 with addition of bromide (200 µg/L) and another set at pH 7 with a temperature of 7°C. Hypochlorite solution was prepared using the Standard Method 4500-Cl B (APHA, 1992). (Chapter 5, Section 5.2.3). The chlorine dose required was determined by preliminary chlorine demand experiments in order to have the free chlorine residual slightly higher than 1 mg/L as $Cl_2$ after seven days of contact time. A 100 mL bottle was partly filled with the water sample, the buffer and the chlorine solution were added and the bottle was filled completely and capped headspace free with a PTFE-lined cap. Samples were incubated for 0.5, 1, 3, 6, 24, 72 and 168 hours at 20°C in the dark with the exception of the samples incubated at 7°C. At the end of the incubation period the chlorine residual was measured using Iodometric Method I (APHA, 1992) and a sulphur-reducing agent (sodium sulphite) at a concentration of 100 g/L was added to the samples to destroy the chlorine residual whilst not degrading the five HAAs measured (MBAA, DCAA, TCAA, BCAA and DBAA) (Singer et al., 2002). Samples were prepared in duplicate independently.

Chloraminated samples were prepared with two different ratios of preformed chloramines: $Cl_2$:N: 3:1 and 7:1. Two different pHs were investigated: pH 6 and 8, both at 20°C for 168 hours. Chloramine residual was measured using the method 4500-Cl F. DPD Ferrous Titrimetric Method (APHA, 1992). Samples were prepared in duplicate independently.

#### *6.2.3.2 Quality control samples*

5 mg/L chlorine dosing solution was put into 100 mL glass bottle PTFE-lined screw cap with pure water. Appropriate amounts of buffer to adjust the pH to 6, 7 and 8 were added. Then the bottle was filled with pure water and stored with the samples at 20 ºC for up to seven days.

#### *6.2.3.3 Sample preparation for the determination of HAA precursors*

Fractions were first dried to remove any acetonitrile left in the samples. Then they were regenerated with a solution of 0.1 M sodium hydroxide (NaOH) and their NPOC was measured. Then they were chlorinated in a 100 mL bottle. pH was adjusted in each fraction to 7 ± 0.2 to have comparable results. Fractions were chlorinated with 5 mg/L of sodium hypochlorite for 72 hours and at 20ºC. At the end of the incubation period the chlorine residual was measured using Iodometric Method I (APHA, 1992) and ammonium chloride at a concentration of 100 mg/L was added to the samples to destroy the chlorine residual whilst not degrading the nine HAAs measured in the fractions (Singer et al., 2002). Samples were prepared in duplicate independently.

#### *6.2.3.4 HAA and THM sample preparation*

For the measurement of THMs, 5 mL of water sample was transferred into a 10 mL vial allowing 5 mL of headspace. Following this, the samples were analysed by headspace GC/MS. Samples were prepared in duplicate and analysed in triplicate. HAA samples were first converted to their protonated forms before processing the extraction with organic solvent and deriving to form methyl esters. The method used for the derivatisation was extensively explained in Chapter 3.

For both HAAs and THMs, water samples were extracted without being in contact with disinfectant to determine the natural and anthropogenic presence of THM and/or HAAs.

### 6.2.4 Sample analytical methods

$HAA_5$ measured for the determination of the parameter impact and the modelling study were quantified with an Agilent 6890 GC/ECD available at Open University (Milton Keynes, UK). A volume of 1 µL was injected with the injector at 200°C with a 5:1 split, separation was performed by a BPX5 column (SGE, UK; 30 m × 0.25 mm × 0.25 µm) with a helium carrier gas at a column flow rate of 1.1 ml/min. The initial oven temperature was 35°C followed by a 5°C per minute temperature ramp to 220°C and held for 1 minute. The detector temperature was 230°C and the rate of data collection 20 Hz. This was carried out at the Open University (Milton Keynes, UK).

Instrument conditions for the measurement of $HAA_9$ from the fractionated samples were described in Chapter 3 Section 3.3.1.4.

THMs were analysed using a Varian Saturn 2200 (ion-trap) GC/MS. The samples were heated and agitated by CTC CombiPal to 60°C for 30 minutes. 500 µL of headspace was removed by heated syringe and injected with a 10:1 split, separation was performed by a BPX5 column (SGE, UK; 30 m × 0.25 mm × 0.25 µm) with a helium carrier gas at a column flow rate of 1.1 ml/min. The injector temperature was 250°C; the initial oven temperature was 45°C for 2 minutes followed by a 10°C per minute temperature ramp to 90°C. The MS was operated in the electron ionisation (EI) mode. The ion-trap temperature was set at 230°C and the electron energy was 70 eV. Mass spectra were collected in full scan mode (33-300 amu). The ions of 83, 129 and 173 m/z were selected as quantification ions. Quantification of THMs was achieved by comparing the chromatograms of the samples with the calibration curves from standards. THM measurement was carried out at the Open University (Milton Keynes, UK).

## 6.3 RESULTS AND DISCUSSION

### 6.3.1 Water characterisation

Characteristics of the waters are summarised in Table 6.1. The concentration of NOM was greater in the lowland (4.7 mg/L) than in the upland water (2.1 mg/L). NOM fractionation indicated that NOM from the upland water had a higher hydrophilic content than the lowland water which had significant transphilic content (Table 6.1). Hwang et al. (2001) reported that the transphilic fraction of intermediate polarity is generally more hydrophobic than hydrophilic but this statement was highly dependent on the water source.

The reactivity with respect to DBP-FP can be characterised with $SUVA_{254}$ (Edzwald and Tobiason, 1999). A high $SUVA_{254}$ value is an indicator of a high reactivity towards DBP production (Singer et al., 2002). The lowland water had a lower $SUVA_{254}$ value than the upland water (1.3 and 2.3 L/m-mg C respectively), but both waters had overall relatively low $SUVA_{254}$ values as compared to other fresh waters reported in the literature (Edzwald and Tobiason, 1999). In addition, these values were similar to the values found in the same water and studied in Chapter 5 ($SUVA_{254}$ values of 1.6 and 2.6 L/m-mg C for lowland and upland water respectively).

Table 6.1 Water characteristics

| Parameters | Upland water | Lowland water |
|---|---|---|
| pH | 6.7 | 8.0 |
| NPOC (mg/L) | 2.1 | 4.7 |
| $UV_{254}$ (1/m) | 4.8 | 5.9 |
| $SUVA_{254}$ (L/m-mg C) | 2.3 | 1.3 |
| Alkalinity (mg/L of $CaCO_3$) | 6 | 188 |
| Bromide content (µg/L) | 34 | 206 |
| THM-FP[a] (µg/L) | 72 | 89 |
| HAA-FP[a] (µg/L) | 104 | 84 |
| Hydrophobic neutral (%) | 4 | 2 |
| Hydrophobic acid (%) | 19 | 23 |
| Transphilic (%) | 8 | 31 |
| Hydrophilic base (%) | 2 | 4 |
| Hydrophilic acid + neutral (%) | 67 | 40 |

[a] Experimental conditions: pH = 7, temperature = 20°C and contact time with chlorine = 168 hours.

As expected, the two waters differed not only in their alkalinity but also in their bromide concentration. The bromide concentration of the lowland water (206 µg/L) was

six times higher than that of the upland water (34 µg/L). It is therefore likely that the lowland water will produce more brominated species.

$HAA_5$ (MBAA, DCAA, TCAA, BCAA, DBAA) and $THM_4$ concentrations were similar in the lowland water after 168 hours contact time at pH 7, whereas the upland water had the potential to form more $HAA_5$ than $THM_4$. Same trend was observed in Chapter 5 for the nine HAAs after 24 hours exposure to chlorine. It should be considered that the quantification of the three remaining HAAs (not measured here) might contribute to higher concentration of the total HAA in the lowland water considering the high level of bromide. For example in Chapter 5, it was observed that after 24 hours contact time with chlorine, $HAA_3$ (BDCAA, DBCAA and TBAA) contributes to 27% of the total HAA in the lowland water, but only 7% in the upland water. Malliarou et al. (2005) found that some regions of the UK produced an average total level of THMs higher than the HAAs, while the contrary was found in other regions. This highlights the differences observed in different geographical locations in the UK.

### 6.3.2 Parameters affecting the formation of HAAs and THMs

#### *6.3.2.1 Impact of pH*

It is well known that the formation of DBPs is strongly dependent on the pH set while using chlorine as to disinfect (Krasner, 1999; Singer, 1999; Xie, 2003). Here it has been shown (Figure 6.4) that increasing pH from 6 to 8 decreased $HAA_5$ in the lowland water by 15%. DCAA and BCAA were found to be more affected by pH than TCAA. DCAA and BCAA concentrations at pH 8 were significantly lower than at pH 6 and 7. Liang and Singer (2003) reported that increasing pH from 6 to 8 had a very little effect on the formation of the MXAA and DXAA species, but significantly decreased the formation of the TXAA species. In the literature, DCAA formation was reported to be highest at pH 7 (Krasner, 1999) which is true of the results found here.

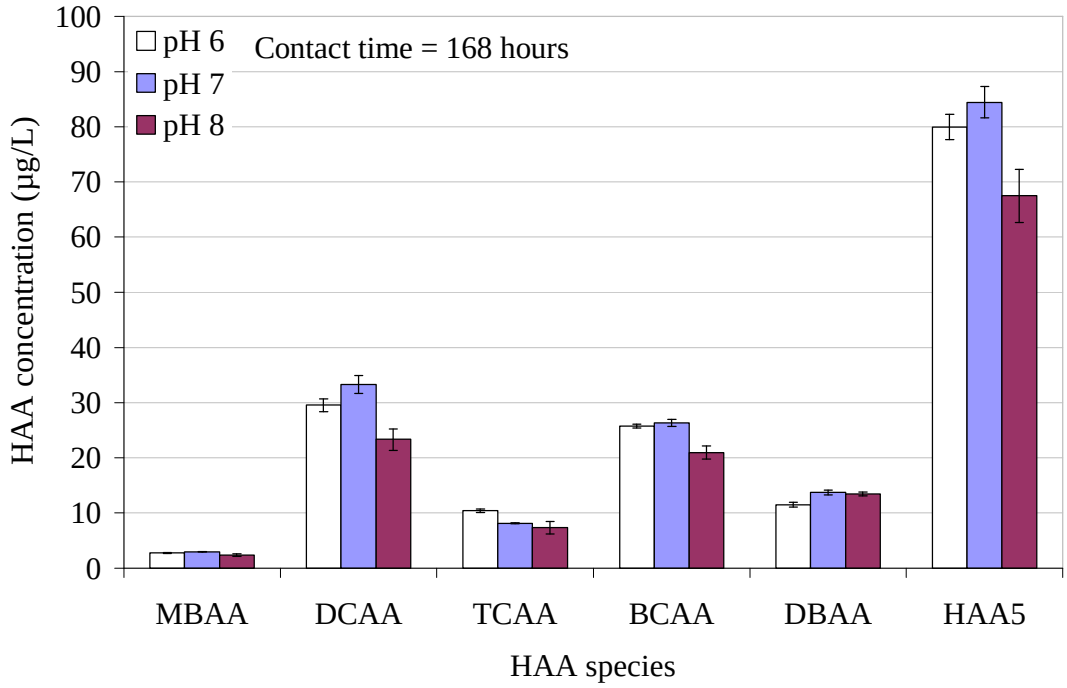



Figure 6.4 Comparison of pH effect on the formation of measured $HAA_5$ in the lowland water

For the upland water $HAA_5$ formation was 14% greater at pH 6 than at pH 8 and the lowest concentration was found at pH 7 (Figure 6.5). In the upland water, only TCAA, DCAA and BCAA were detected due to the low bromide content in this water. The DCAA concentration was higher at pH 6 and similar at pH 7 and 8. TCAA increased by 28% with increasing pH, which is contrary to the literature (Liang and Singer, 2003; Zhuo et al., 2001) and the results found for the lowland water.

The contradictory results found here were believed to be a result of the difference of NOM present in the waters. Although Singer et al. (2002) concluded that precursors for MXAA, DXAA and TXAA were different, here it can be concluded that the precursors of DXAA and TXAA did not react with chlorine in a similar way from one source to another. This would suggest that the precursors between sources could have the same base chemical structure, but may have different functional groups attached to this base and therefore the pH did not promote the oxidative cleavage of the functional group the same way between sources, which could induced the contradictory results observed here.

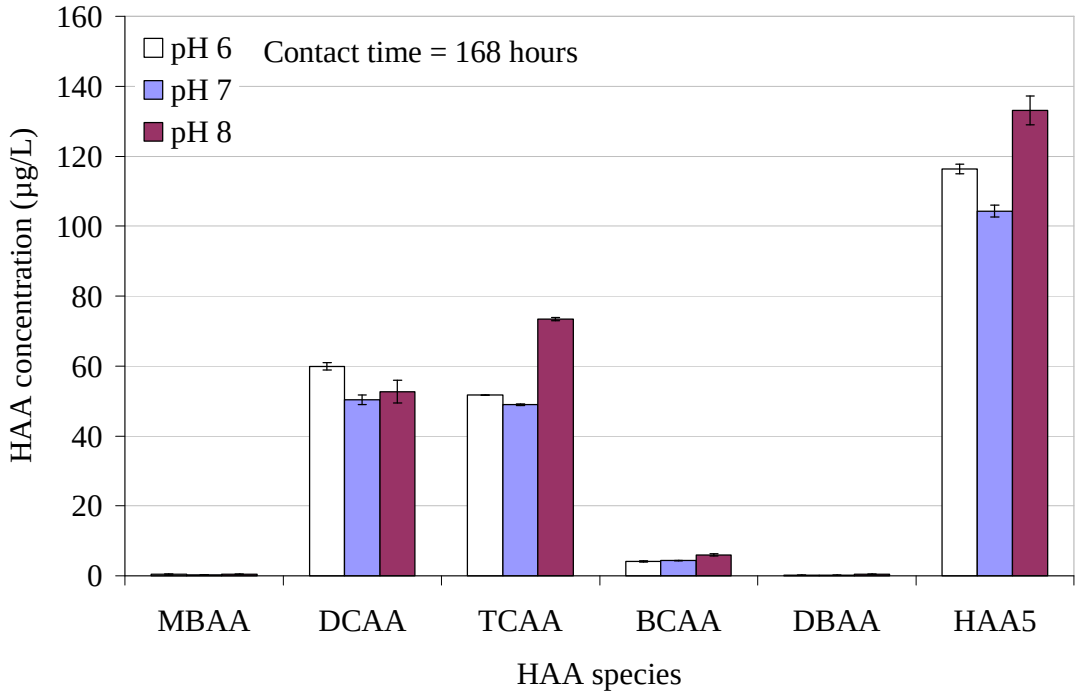



Figure 6.5 Comparison of pH effect on the formation of measured $HAA_5$ in the upland water

Trussell and Umphres (1978) reported that the formation of THMs consists of alternate hydrolysis and halogenation steps. All these reactions are favoured under alkaline condition, thus more THMs are formed at higher pH, which is illustrated by the results found here after 168 hours exposure to chlorine (Figure 6.6). The impact of pH is limited in the upland water (not shown) compared to the lowland water which could be explained, again, by the difference of NOM responsible for the THM formation and its likelihood to undergo hydrolysis and halogenation reactions.

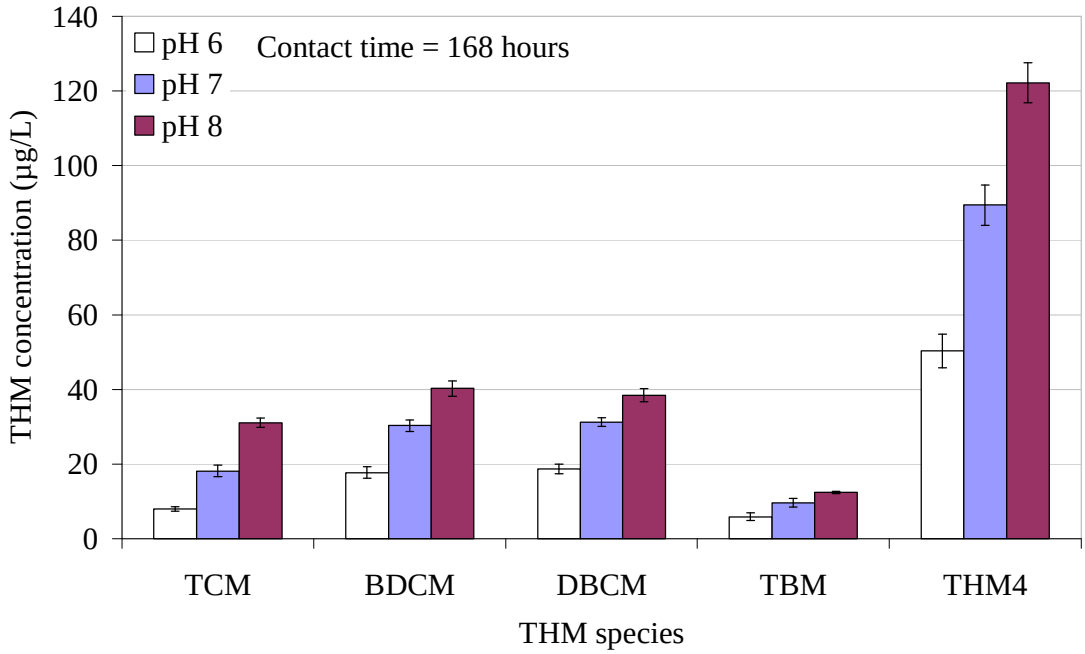



Figure 6.6 Comparison of pH effect on the formation of $THM_4$ in the lowland water

Because the impact of pH is equivocal on the formation of HAAs, but well defined on the formation of THMs, it cannot be concluded here if there is a link between the HAA and THM precursors. The impact of pH combined with the impact of contact time will be modelled in the Section 6.3.4.

#### *6.3.2.2 Impact of bromide*

The effect of bromide concentration on HAA and THM formation and speciation was investigated by spiking the lowland and the upland water with 200 µg/L of bromide. In the lowland water, the addition of bromide had a slight impact (10% decrease) on the total concentration of HAA measured. Less DCAA and TCAA were formed, whereas more brominated HAA species were produced as expected. The addition of bromide had a greater impact in the upland water than in the lowland water. With the upland water the concentration of $HAA_5$ decreased (Figure 6.7) with a switch from DCAA and TCAA to brominated species MBAA, BCAA and DBAA.

It was reported by Hua et al. (2006) that the total concentration of the five regulated HAAs in the US (MCAA, MBAA, DCAA, TCAA and DBAA) decreased as bromide concentration increased because of the number of brominated species measured. This applies here but the exception is that BCAA is included in the total HAA and not MCAA. However the same study reported that addition of bromide increased the total $HAA_9$ yield between 0 and 35%.

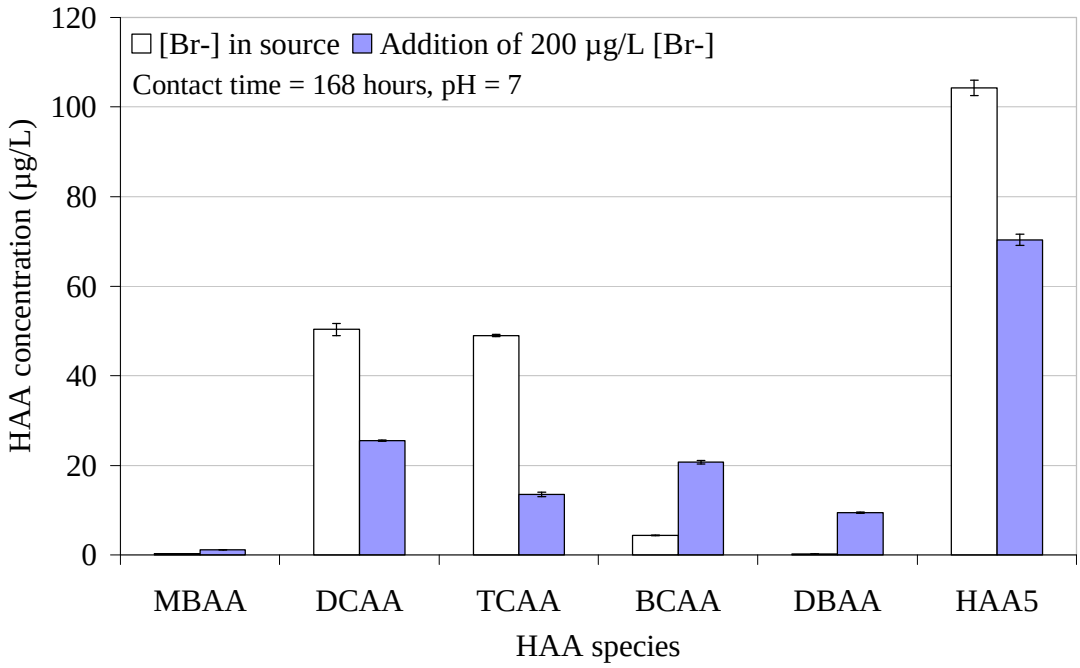



Figure 6.7 Impact of bromide on the formation of measured $HAA_5$ in the upland water

Bromine was reported by Cowman and Singer (1996) to be more reactive than chlorine in substitution and addition reactions that form HAAs, thus the inclusion of bromine shifts the speciation of the HAA towards the brominated species. Here, the difference observed in bromide incorporation is likely to be due to the number of HAA species measured.

The formation of THM is also affected by the addition of bromide. Hua et al. (2006) reported that increasing initial bromide levels resulted in a substantially increased THM molar concentration between 14% and 74%. Here the total THM weight concentration increased by 60% in the lowland water and by 54% in the upland water. In the upland

water, only the brominated species increased, whereas all the brominated species and TCM were augmented in the lowland water.

#### *6.3.2.3 Impact of temperature*

Reducing the incubation temperature from 20°C to 7°C, resulted in a reduction of both HAAs and THMs. The concentration of HAAs and THMs dropped by 59% and 43% respectively in the lowland water (Figure 6.8) and by 43% and 53% respectively in the upland water.

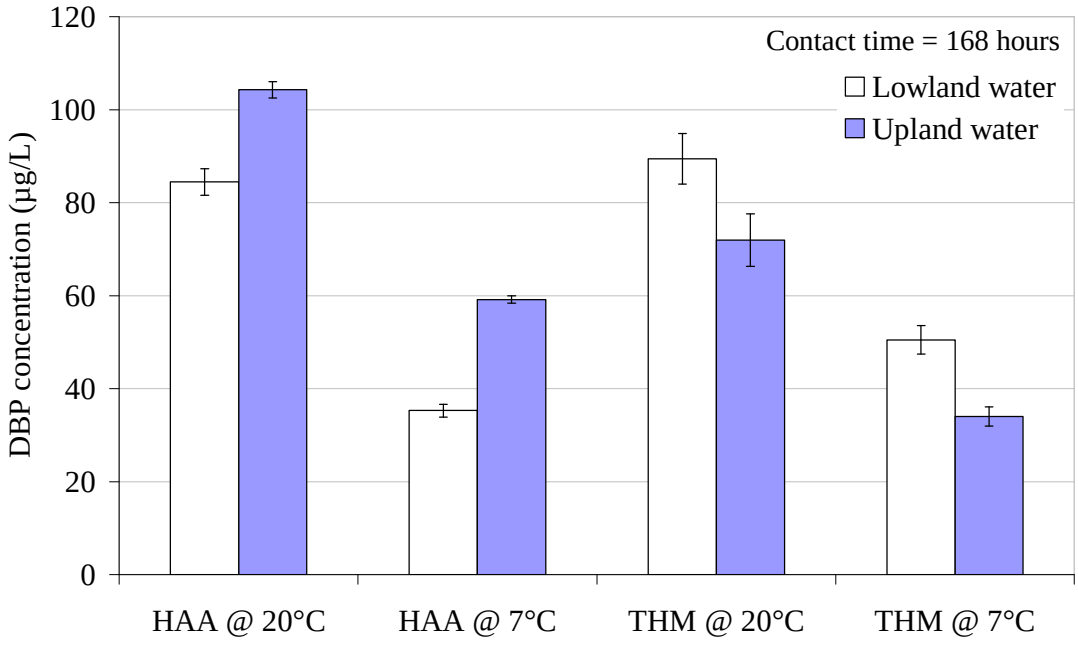



Figure 6.8 Temperature effect on the DBP-FP in lowland and upland water

El-Dib and Ali (1995) reported that the effect of temperature (rise between 0 and 30°C) on the THM yield was rather limited compared with data reported by other investigators (Urano and Takemasa, 1986) and concluded that the differences were due to the nature of organic precursors liable to be found in the water.

Dojlido et al. (1999) reported that the concentrations of HAAs were seasonally dependant. During the winter season (1°C) they found levels of ~ 0.63 µg/mg C whereas in the summer (23°C), concentrations reached ~ 7.4 µg/mg C. In the UK, the

effect of season on HAA formation has not been determined but the results shown here (Figure 6.8) indicate there may be a seasonal effect.

#### *6.3.2.4 Impact of reaction time*

The rate of DBP formation (Figure 6.9) was characterised by a general trend of an initial rapid reaction during the first few hours, followed by a steady rate of increase over the 168 hours of contact time with chlorine, and this agrees with Reckhow et al. (1990) and Singer et al. (2002). After six hours of reaction, up to 30 and 40% of the reaction has been completed for the lowland and upland water respectively, increasing to 50 and 65% after 24 hours, again for the lowland and upland water respectively. Singer et al. (2002) reported that as long as NOM and free chlorine were present, both HAAs and THMs would continue to form. The µg levels of HAA and THM formed per mg of NPOC were respectively 2.8 and 1.8 greater in the upland water than in the lowland water after 168 hours contact time with chlorine, despite the fact that the NPOC of the upland water was 2.1 mg/L and the one of the lowland water was 4.7 mg/L (Figure 6.9). This is confirmed by Peters et al. (1991), who reported that water from a surface river with a DOC value of 4.6 mg/L produced 3.8 µg/L total HAA, whereas they found other surface water with a DOC of 2.7 mg/L forming 10 µg/L total HAA, highlighting the water specificity of NOM reactivity. Presently, the NOM available in the treated lowland water showed similar $HAA_5$ and $THM_4$ outcome when in contact with chlorine, whereas in the upland water, the $HAA_5$ formed faster at the beginning of the reaction than the $THM_4$. For example after six hours of contact time with chlorine the upland water exhibited a $HAA_5$ concentration (20 µg/mg C) 1.7 greater than the $THM_4$ concentration (12 µg/mg C). It could be deduced that the reactive site of NOM from each water differed. In addition, the difference observed between the two waters is also believed to be due to the number of HAAs measured. Here, five HAAs are quantified; however, lowland water has high level of bromide, which can account for more brominated species, not quantified here. Furthermore, the result obtained here for the $HAA_5$ after 24 hours contact time with chlorine tallied with the results found in Chapter 5 for the five HAAs. Therefore, the reactivity of NOM remains similar between water collected in 2006 and 2008.

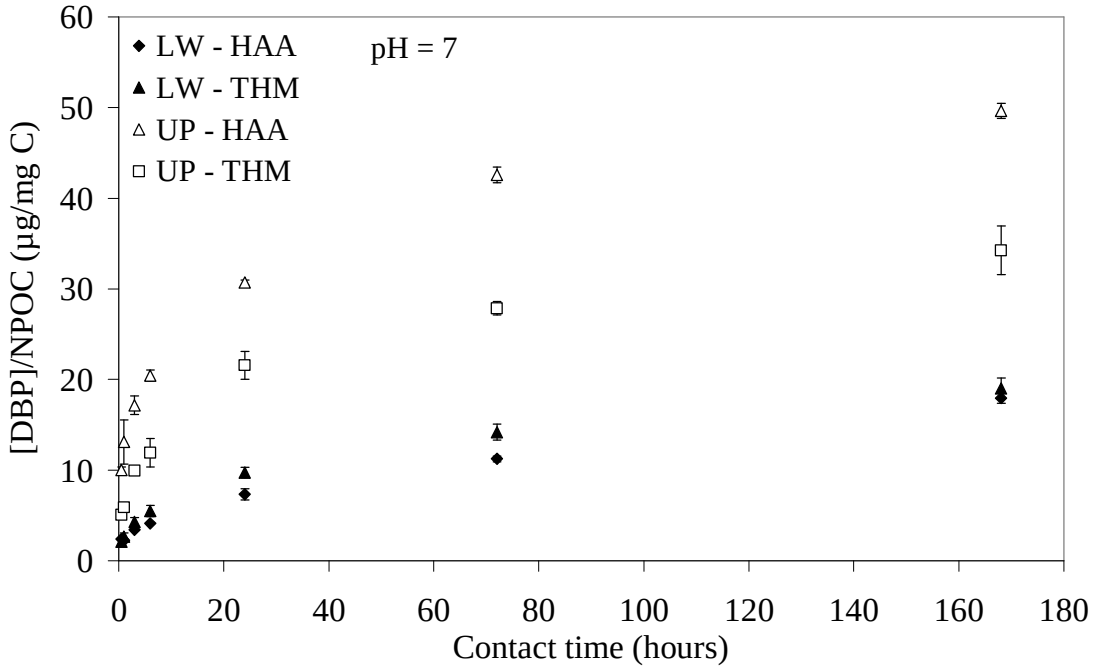



Figure 6.9 Impact of chlorine contact time on $HAA_5$ and $THM_4$ formation from lowland water (LW) and upland water (UW), experimental conditions: pH = 7°C, temperature = 20°C, NPOC of lowland water = 4.7 mg/L and upland water = 2.1 mg/L

#### *6.3.2.5 Impact of disinfectant*

The impact of switching from chlorine to chloramines in both waters is presented in Figure 6.10 and Figure 6.11. As shown, pH 6, pH 8 and two chlorine to nitrogen ratios ($Cl_2$:N) of 3:1 and 7:1 for the preformed chloramines have been investigated after 168 hours contact time with the disinfectant. Firstly, there was a considerable decrease of total HAA in both waters when using chloramines as an alternative to chlorine. In the lowland water, total HAA formation decreased between 82 to 92% (Figure 6.10), which is similar to the decrease observed in the upland water between 86 to 94% (Figure 6.11). These values compare well with Cowman and Singer (1996), who reported a reduction on the order of 90 to 95%, when using chloramines instead of chlorine. In any case, here, waters exposed to preformed chloramines did not form more than 20 µg/L total HAA, whereas it was observed the lowland and the upland water exposed to chlorine could form up to 80 and 133 µg/L of $HAA_5$ respectively. In the lowland water (Figure 6.10), the major decrease was obtained at pH 6 and with the $Cl_2$:N ratio 3:1, whereas in the upland water (Figure 6.11), this was at pH 8, with the same $Cl_2$:N ratio of 3:1. Diehl

et al. (2000) reported that HAA concentration in general decreased as the pH increased (here, pH 8) and the $Cl_2$:N ratio decreased (here, ratio 3:1). Here the results agree for the upland water, whilst the contrary to Diehl et al. (2000) was found for the impact of pH in the lowland water. The impact of pH was reported to be equivocal in Section 6.3.2.1 and can explain the difference observed between waters and with Diehl et al. (2000). However, the chloramine chemistry is well known. A $Cl_2$:N ratio of 7:1 is close to the breakpoint chlorination and, therefore, the species present are a mixture of monochloramine, dichloramine and free chlorine. It is the free chlorine, which can be responsible for more HAA formed at the $Cl_2$:N ratio of 7:1, whereas at a $Cl_2$:N ratio of 3:1, only monochloramine is present (Wolfe et al., 1984) and the lack of free chlorine is the reason for the low formation of HAAs, as it has been pointed out by Diehl et al. (2000).

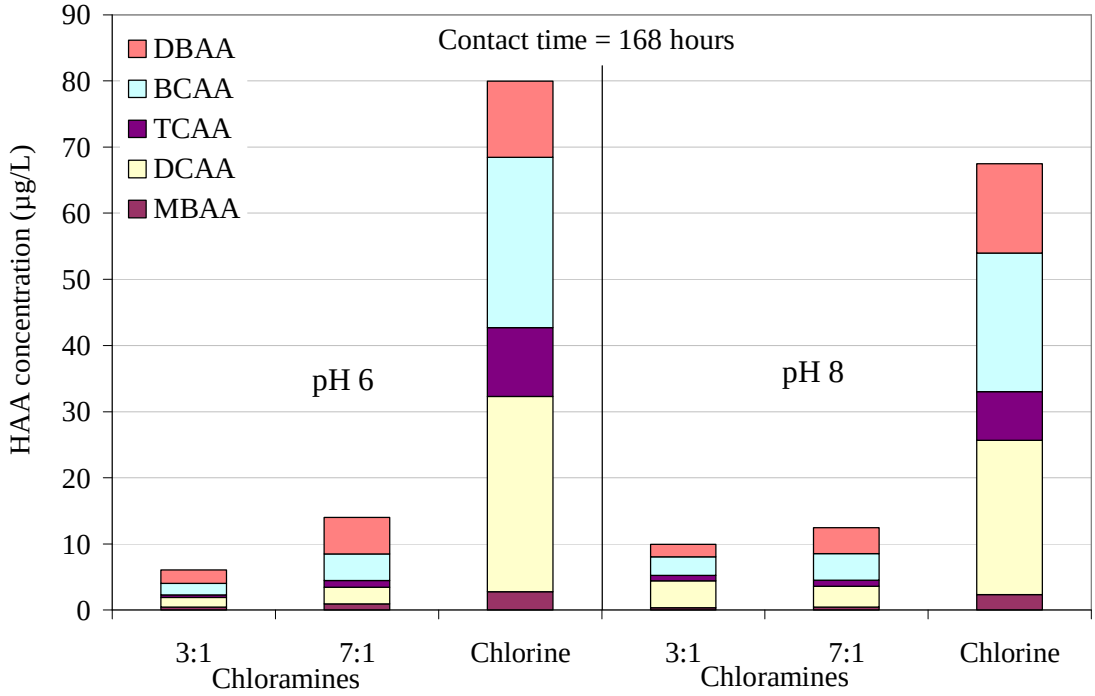



Figure 6.10 Comparison of chlorine versus chloramines in lowland water, at pH 6 and pH 8; $Cl_2$:N ratio = 3:1 and 7:1, contact time = 168 hours

The major species detected with chloramines were the DXAAs in both waters, with a contribution between 86 to 95% of the total HAA at both pHs, both ratios. This is in line with Diehl et al. (2000), who also reported DXAA to be the dominant HAA species,

comprising between 70 to 100% of the total $HAA_6$ ($HAA_5$ + MCAA). The difference observed between the two waters, here, consists of the speciation of the DXAAs. In Chapter 5, Section 5.3.2.1, the BIF was introduced and it characterises the degree of bromine substitution. Here, the lowland and the upland water had 206 and 34 µg/L of bromide respectively. Therefore after exposure to chloramines, BIFs were significantly different from lowland to upland water. For example, BIF values ranged from 0.53 to 0.99 for the lowland water, whereas they ranged from 0.03 to 0.16 in the upland water. The values of BIF compare well with Pope et al. (2006), who also reported higher BIF into DXAA formed with chloramines, when the water source had higher level of bromide. For example, they reported a BIF of 0.5 for a bromide level of 168 µg/L, and a BIF of 0.06 for a water with a level of bromide of 33 µg/L. Therefore, this explained here the greatest formation of brominated DXAA (BCAA and DBAA) (48 to 68%) in the lowland water than in the upland water (3 to 18%). Consequently in the upland water, the major species was DCAA comprising more than 90% of the species formed with chloramines.

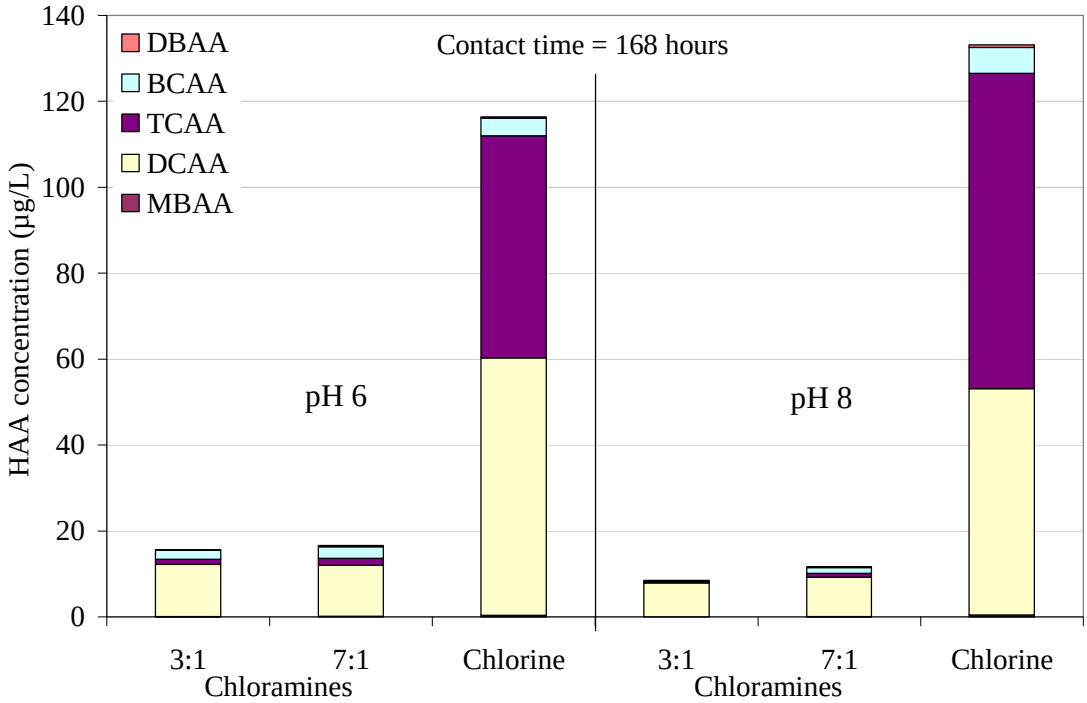



Figure 6.11 Comparison of chlorine versus chloramines in upland water, at pH 6 and pH 8; $Cl_2$:N ratio = 3:1 and 7:1, contact time = 168 hours

The effect of using chloramines instead of chlorine was also investigated on the formation of $THM_4$ after 168 hours contact time with the disinfectant. The results from Table 6.2 showed that THM concentrations decreased between 75 and 98% in the lowland water and between 92 to 95% in the upland water. The concentrations of THMs measured in the lowland water were lower than 15 µg/L at any pHs and ratios and were lower than 3 µg/L in the upland water. Chloramines limit the free chlorine contact time and therefore induce a considerable reduction of THM as explained by Carlson and Hardy (1998).

Table 6.2 Decrease of $THM_4$ in chloraminated lowland and upland water compared to the same chlorinated sample; contact time with chloramines = 168 hours

| | Decrease of $THM_4$ in chloraminated water vs. chlorinated water (%) | | | |
|---|---|---|---|---|
| | Lowland water | | Upland water | |
| $Cl_2$:N ratio | pH 6 | pH 8 | pH 6 | pH 8 |
| 3:1 | 88 | 98 | 95 | 98 |
| 7:1 | 75 | 88 | 92 | 98 |

### 6.3.3 HAA precursor investigation

To aid the water companies to better control the DBPs, it was important to determine their precursors in order to develop possible options for the precursor removal. While all the previous work focused on five HAAs, it is important to specify that here the nine HAAs have been measured, because $HAA_9$ standards were simply available as a mixture at the time of the experiments.

As explained earlier, the waters fractionated here were originally treated and were therefore more hydrophilic in content. The fraction mass distribution of NPOC was again presented in Table 6.3, and was explained earlier in Section 6.3.1. Results presented in Table 6.3 showed that the individual NPOC fraction values were relatively low, when doing the 72 hours FP test with chlorine. Moreover, HAA concentrations were standardised with the NPOC values to have the best comparison between fractions.

Each fraction was evaluated for its chlorine demand. Results available for the lowland water (Table 6.3) showed that it was the transphilic fraction that was the most active in consuming chlorine, whereas the hydrophobic acid and hydrophilic acid + neutral fractions consumed similar quantity of chlorine (1.3 mg/mg C). In the upland water, the transphilic and the hydrophobic neutral fraction were the most active fractions towards

the chlorine demand (2.6 mg/mg C), followed by the hydrophobic acid (1.9 mg/mg C) and the hydrophobic base equivalent to the hydrophilic acid + neutral (0.8 mg/mg C). This differs with the results reported by Hwang et al. (2001) in which the order of reactivity of the NOM fractions towards the chlorine demand was hydrophilic base >> hydrophilic acid + neutral > transphilic ~ hydrophobic. However, in the literature, Croué et al. (2000) reported that in filtered waters, the transphilic fraction was the most active in consuming chlorine and that all the other fractions had a chlorine demand values of 1 ± 0.2 mg/mg C, which showed that these values were water specific, because the precursors differ from one source to another and also explained why the chlorine demand was not similar between the lowland and the upland water. Analysis of molecular weight showed similar trend between the two waters (Table 6.3), which indicates that the molecular weight of the fractions was not related to their reactivity with chlorine.

Table 6.3 Summary of NOM fraction properties in lowland and upland water

| | HPO-N | HPO-A | TPI | HPI-B | HPI-A+N |
|---|---|---|---|---|---|
| *Lowland water* | | | | | |
| Fraction mass distribution of NPOC (%) | 2 | 23 | 31 | 4 | 40 |
| NPOC fraction [a] (mg/L) | 1.9 | 1.0 | 1.7 | 1.0 | 1.4 |
| Chlorine demand (mg/mg C) | NA [c] | 1.3 | 2.6 | NA [c] | 1.3 |
| DXAA/TXAA ratio | 1.5 | 1.1 | 2.6 | 1.0 | 2.2 |
| Molecular weight [b] | HPO-A ~ TPI > HPO-N ~ HPI-B | | | | NA [c] |
| *Upland water* | | | | | |
| Fraction mass distribution of NPOC (%) | 4 | 19 | 8 | 2 | 67 |
| NPOC fraction [a] (mg/L) | 0.9 | 1.2 | 1.4 | 0.5 | 2.5 |
| Chlorine demand (mg/mg C) | 2.6 | 1.9 | 2.6 | 0.8 | 0.8 |
| DXAA/TXAA ratio | 0.9 | 0.6 | 0.9 | 1.0 | 1.7 |
| Molecular weight [b] | HPO-A > TPI > HPO-N ~ HPI-B | | | | NA [c] |

[a] Corresponds to the NPOC values of the fractions when doing experimental analyses; [b] Measured with high performance size exclusion chromatography (HPSEC) (Shimadzu, Milton Keynes, UK); [c] Not analysed.

Nine HAAs were measured from each fraction and the concentrations in µg/mg C were presented in Figure 6.12. Concentrations of $HAA_9$ ranged from 14 to 41 µg/mg C in the lowland water and from 7 to 72 µg/mg C in the upland water. The order of reactivity of the five NOM fractions with respect to formation of $HAA_9$ was as follow:

- Lowland water: HPI-B > TPI > HPI-A + N > HPO-A > HPO-N

- Upland water: HPO-A > HPO-N > TPI > HPI-A + N > HPI-B

Note: HPO-N = hydrophobic neutral; HPO-A = hydrophobic acid; TPI = transphilic; HPI-B = hydrophilic base and HPI-A +N = hydrophilic acid + neutral.

These results indicated a major difference of precursor reactivity towards the HAAs between the lowland and the upland water. Hwang et al. (2001) concluded that the reactivity of the hydrophilic base could be variable depending on the water source, but found a general order of fraction reactivity being hydrophilic acid + neutral > transphilic ~ hydrophobic. Marhaba and Van (2000) reported that the most reactive fraction was the hydrophobic neutral in filtered water. Therefore, fraction data varied considerably between sources.

HAA speciation was also studied from each fraction. It was clear from the Figure 6.12 that most of the bromide was present in the last two fractions (hydrophilic base and hydrophilic acid + neutral). The ratio DXAA:TXAA (also reported in Table 6.3) showed a predominance of DXAA species in the lowland water, whereas this was variable in the upland water. For example, the ratio was 0.6 for the hydrophobic acid in the upland water, indicating a dominance of TXAA, and especially TCAA, whereas this ratio was 1.7 in the hydrophilic acid + neutral fraction, but this can be explained by the presence of bromide in the fractions, which is responsible for the decrease of TCAA (explained in the Chapter 5, Section 5.3.2.1). The predominance of DXAA in the lowland water and specifically in the transphilic and hydrophilic acid + neutral is believed to be caused by the presence of algae in the water source. Indeed, proteins and polysaccharides, present in these two fractions (Hwang et al., 2001), are the main component of extracellular organic matter (EOM) of *Anabaena flos-aquae*, a common blue-green algae found in reservoirs (Huang et al., 2008). Huang et al. (2008) reported that EOM formed predominantly DXAA, when the algae were in their death phase.

No trend could be observed between the ratio DXAA:TXAA. Whilst, it was found that DXAA correlated well with TXAA in the upland water ($R^2 = 0.93$), no correlation could be found in the lowland water. Hwang et al. (2001) found the order of DXAA:TXAA ratio to be transphilic > hydrophobic and that the DXAA:TXAA ratio was variable between water source, which tends to be similar to the results found here.

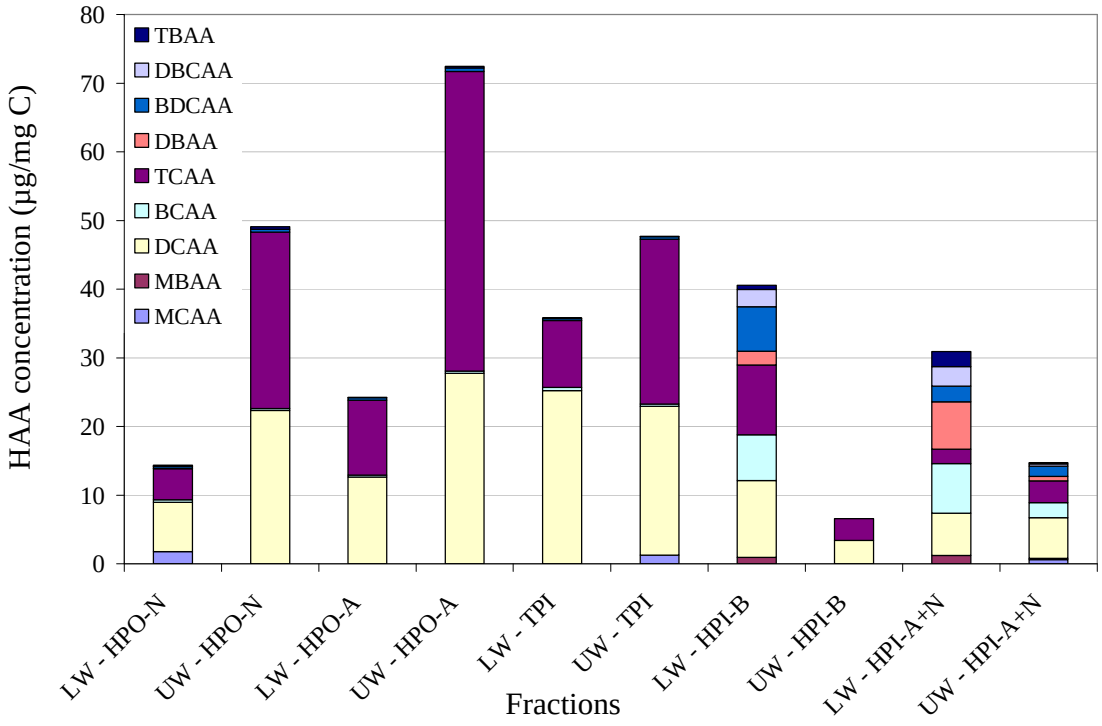



Figure 6.12 HAA concentrations from lowland water (LW) and upland water (UW) from five different fractions; experimental conditions: pH = 7, contact time = 72 hours, temperature = 20°C

The results found previously are based on the level of HAAs formed per mg of carbon, however, each fraction contributed to a different percentage of the mass distribution of NPOC and therefore, it was necessary to consider the real percentage of the $HAA_9$, which is based on the concentration of $HAA_9$ in µg/mg C multiply by the contribution of the specific fraction to the fraction mass distribution of the total NPOC. Results are presented in Figure 6.13 and showed that the fractions that contribute the most to the formation of $HAA_9$ in the lowland and upland water were the hydrophilic acid + neutral (40%) and the hydrophobic acid (37%) respectively. Also in the lowland and upland water, the transphilic also contributed 36% and 28% of the formation of $HAA_9$ respectively. These results are based on one sample from each source; therefore, more work should be done to confirm the results found here in order to help the water companies tackle the right fractions when considering precursor removal.

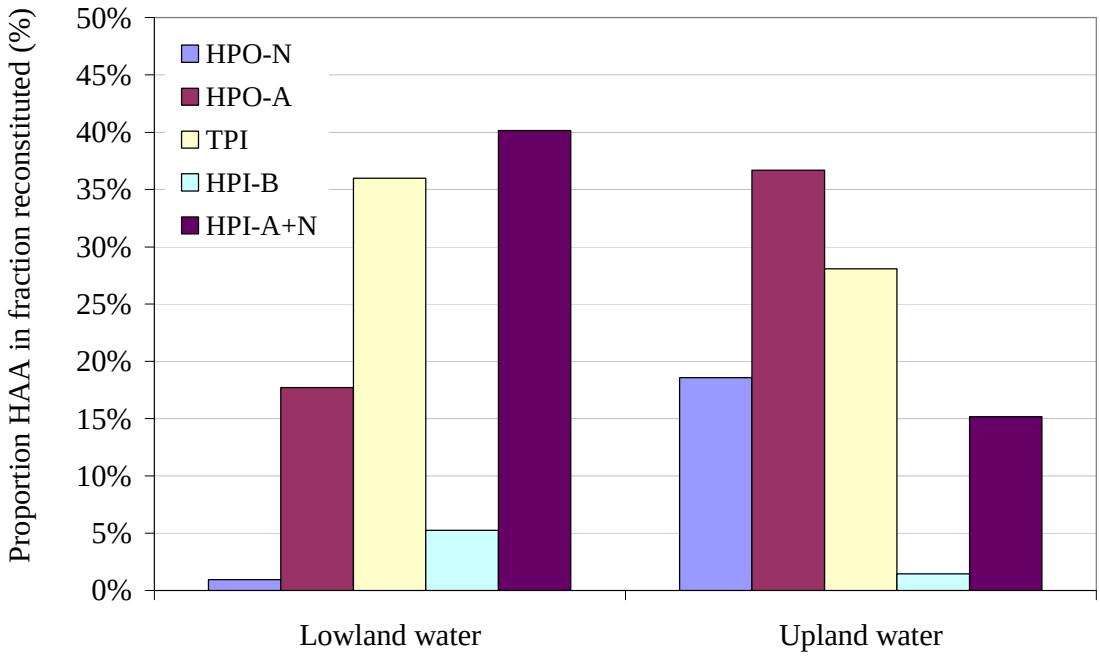



Figure 6.13 Fractions to be targeted for their removal

### 6.3.4 Modelling of the chlorine decay and prediction of $HAA_5$ and $THM_4$

As a result of the complex nature of DBP precursor compounds and their corresponding reactions with disinfectants, models for the quantification of DBPs have been largely developed using empirical approaches (Westerhoff et al., 2000). In the present study, chlorine decay over time has been measured for the lowland and the upland water at three different pHs. Gang et al. (2002) proposed an empirical mathematical model of chlorine decay, from which it is possible to predict THMs and HAAs, but under the specific conditions of pH 8 and temperature of 25ºC. Therefore, it was interesting to see if this model could first, fit the present data and secondly, to test if the model was appropriate outside the experimental conditions specified above.

#### *6.3.4.1 Chlorine decay data modelling*

The mathematical expression development and the assumptions on which the model is based are reported in a study of Gang et al. (2002). To summarise, it was assumed that the formation of DBPs results in two parallel reactions, one with a rapid rate of chlorine decay and the other a slower, long term chlorine consumption. Others assumptions were

that the rate of reaction for each chlorine-consuming reaction was first order in chlorine concentration, that the chlorine demand was solely attributed to the reaction with NOM and proportional to the formation of DBPs.

The parallel first order reaction model used to evaluate the chlorine decay was the following:

$$C(t) = C_0\left\{fe^{-k_R t} + (1-f)e^{-k_S t}\right\}, \qquad \text{Equation 6.2}$$

where C(t) is the chlorine concentration at any time t (mg/L); $C_0$ the initial chlorine concentration dose to give the chlorine residual of at least 1 mg/L after seven days of reaction; f the fraction of the chlorine attributed to the rapid reaction; $k_R$ the first order rate constant for the rapid reaction ($h^{-1}$); $k_S$ the first order rate constant for the slow reaction ($h^{-1}$). The parameters f, $k_R$ and $k_S$ were determined with non-linear regression analysis using the software SPSS version 17.

Data from Figure 6.14 A+B showed that the chlorine decay was rapid during the first six hours of the reaction followed by a more gradual decay, and this at pH 6, 7 and 8. Attempts were then made to fit the chlorine decay data to the parallel first order reaction model. Lines in Figure 6.14 A+B, representing the models, showed that the model fitted the data, generating $R^2$ between 0.956 and 0.997 (Table 6.4). Therefore, the model proposed by Gang et al. (2002), can be adjusted to any type of waters (lowland, upland) and at any pHs.

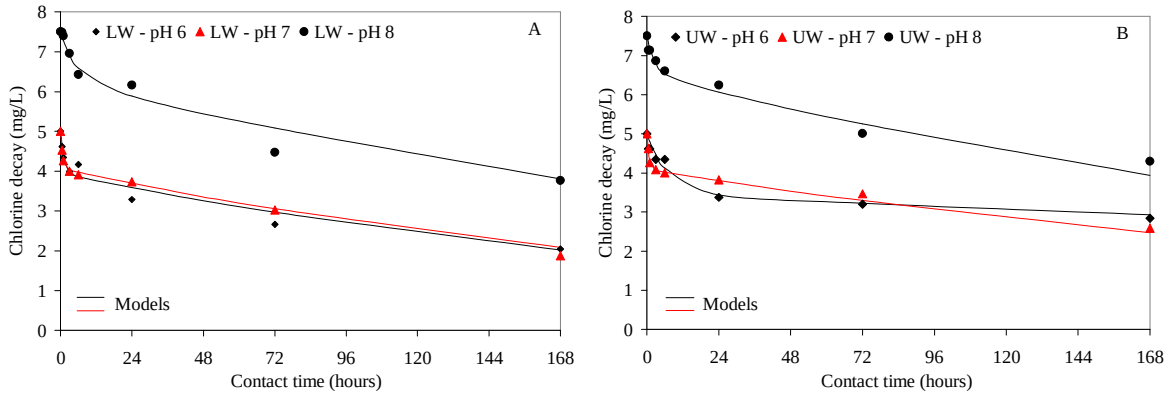



Figure 6.14 Chlorine decay data of (A) lowland water (LW) and (B) upland water (UW), both at pH 6, 7 and 8 fitted to parallel first order reaction model

The reaction constants and other parameters are shown in Table 6.4. The values $k_R$ for all pHs ranged from 0.183 to 1.431 $h^{-1}$ for the lowland water and from 0.135 to 1.294 $h^{-1}$ for the upland water. In both waters, the rate of chlorine decay during the first phase of the reaction was the fastest at pH 7, but no explanation was found as to why the rate of chlorine decay was the fastest at pH 7. The values $k_S$ ranged between 0.001 and 0.004 and were not affected by the pH. The constants of rapid first order decay rate ($k_R$) were always greater than the constants of slower first order decay rate ($k_S$). This is in line with Gang et al. (2003), who also reported $k_R$ being 90 to 150 times larger than $k_S$. Here, for example, at pH 7, $k_R$ was about 350 and 430 times larger than $k_S$ for lowland and upland water respectively. Then the ratios $k_R/k_S$ were the greatest at pH 6 and then pH 8 for both waters, indicating that the pH had an impact on the chlorine decay rate.

The f values, which represent the fraction of chlorine attributed to the rapid reaction, ranged from 0.307 to 0.131, with the greatest values at pH 6, then pH 7 and pH 8. Therefore, the chlorine consumption during the rapid reaction increased with decreasing pH. Between 15 to 30% of the chlorine consumed was attributed to the rapid reaction, which suggested that between 70 to 85% of the NOM reactivity was attributed to the slow reaction, which agrees with Gang et al. (2003), who also reported a value of 70% for three different fractions.

Table 6.4 Lowland and upland water chlorine decay constants for parallel first order reaction model

| Waters and conditions | $k_R$ ($h^{-1}$) | $k_S$ ($h^{-1}$) | f | $R^2$ |
|---|---|---|---|---|
| LW[a] – pH = 6 – T = 20°C | 0.874 | 0.004 | 0.209 | 0.996 |
| LW – pH = 7 – T = 20°C | 1.431 | 0.004 | 0.185 | 0.997 |
| LW – pH = 8 – T = 20°C | 0.183 | 0.003 | 0.159 | 0.971 |
| UW[b] – pH = 6 – T = 20°C | 0.135 | 0.001 | 0.307 | 0.956 |
| UW – pH = 7 – T = 20°C | 1.294 | 0.003 | 0.182 | 0.995 |
| UW – pH = 8 – T = 20°C | 0.351 | 0.003 | 0.131 | 0.975 |

[a] Lowland water; [b] Upland water.

As a summary, it was found here that:

- Data fitted well the parallel first order reaction model and this at three pHs.
- The first order rate constant for the rapid reaction $k_R$ was the largest at pH 7, meaning that the chlorine decay was the fastest at pH 7.

- The pH did not impact on the second part of the reaction, which is the slowest one.
- The chlorine consumption during the rapid reaction increased with decreasing pH.

#### *6.3.4.2 Chlorine decay to predict $THM_4$ and $HAA_5$*

The coefficients obtained from the chlorine decay model were used previously by Gang et al. (2002) to predict $THM_4$ and $HAA_9$. Here, it was decided to find out if the coefficients found could be used to predict $THM_4$ and $HAA_5$. Therefore, on the basis on the chlorine decay model, DBP formation can be expressed as follow:

$$THM_4 = \alpha C_0 \left\{1 - fe^{-k_R t} - (1-f)e^{-k_S t}\right\}, \quad \text{Equation 6.3}$$

$$HAA_5 = \beta C_0 \left\{1 - fe^{-k_R t} - (1-f)e^{-k_S t}\right\}, \quad \text{Equation 6.4}$$

where $\alpha$ = the $THM_4$ yield coefficient, defined as the ratio of the concentration of $THM_4$ (µg/L) to the concentration of chlorine consumed (mg/L), and $\beta$ = the $HAA_5$ yield coefficient, defined as the ratio of the concentration of $HAA_5$ (µg/L) to the concentration of chlorine consumed (mg/L). Gang et al. (2002) presented the model mathematical development from the chlorine decay to the model for DBPs. Here, the differences were the number of HAAs to be modelled and the experimental conditions. Gang et al. (2002) modelled nine HAAs. Here an attempt was made to determine if the model could be applied for the five HAAs measured and at pH 6, 7 and 8.

Previously, in Section 6.3.2.4, it has been shown that the formation of THMs and HAAs was characterised by an initial rapid reaction during the first few hours, followed by a steady rate of increase over the 168 hours of contact time with chlorine. This was observed here at any pHs (Figure 6.15 A + B and Figure 6.16 A + B). The impact of pH on THMs and HAAs was explained in Section 6.3.2.1. The aim of this section here was to fit the THM and HAA data to their respective model formation (Equation 6.3 and 6.4). The modelled data represented with lines in Figure 6.15 A + B and Figure 6.16 A + B showed that in general the models followed the formation of HAAs and THMs. The coefficients of correlation $R^2$, presented in the Table 6.5, were found between 0,755 and

0.969, with only two $R^2$ being below 0.900. Gang et al. (2002) found that the formation of THMs and HAAs was accurately simulated by the chlorine demand model in treated waters. Here, the model could fit approximately HAAs and THMs for the two waters and the three pHs studied.

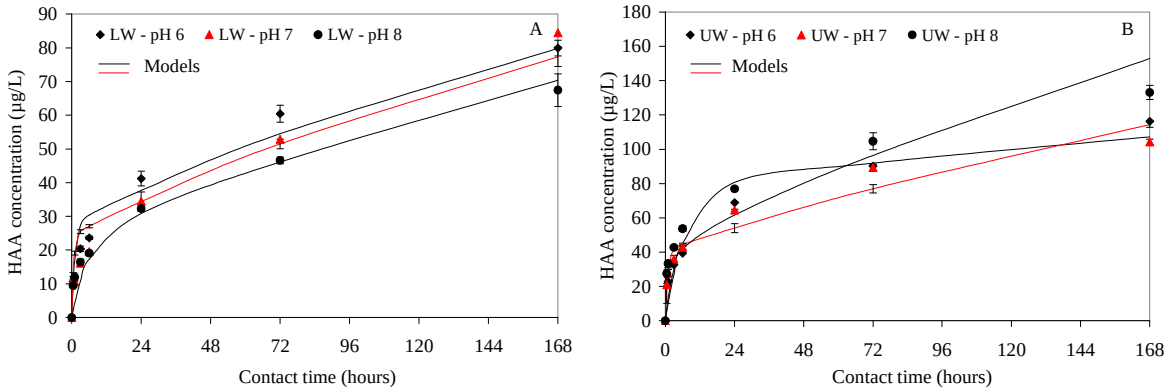



Figure 6.15 $HAA_5$ concentration and formation model predictions for (A) lowland water (LW) and (B) upland water (UW), both at pH 6, 7 and 8

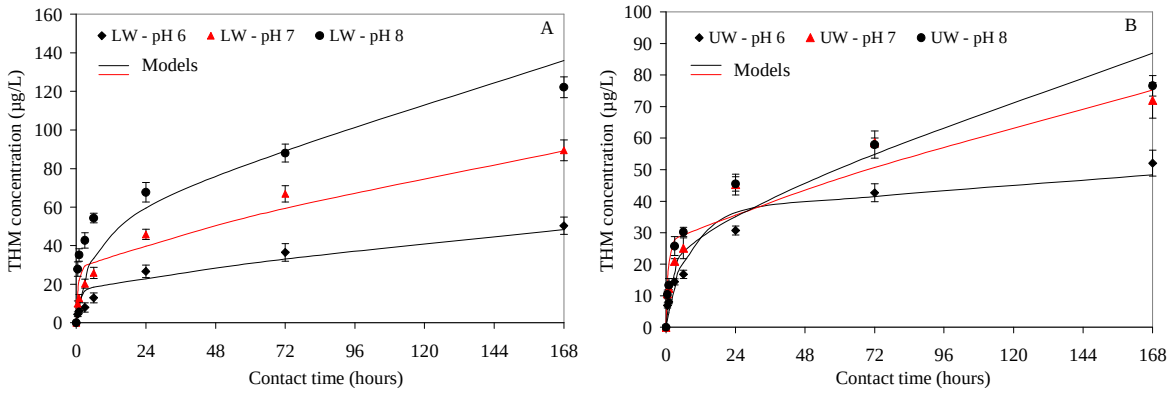



Figure 6.16 $THM_4$ concentration and formation model predictions for (A) lowland water (LW) and (B) upland water (UW), both at pH 6, 7 and 8

The $THM_4$ and $HAA_5$ coefficient yield (α and β respectively), both on a mass basis are shown in Table 6.5. The $THM_4$ coefficient yield α for all waters at three pHs ranged between 16.24 to 36.84 µg $THM_4$ per mg chlorine consumed. This is in line with Gang et al. (2002), who reported the average $THM_4$ yield coefficient of the treated waters to be 30 µg THM per mg chlorine consumed. It was observed that increasing the pH increased α in the lowland water, whereas the pH showed limited impact on α from the upland water, which reinforced this statement already found in Section 6.3.2.1.

The $HAA_5$ coefficient yield β found were between 19.01 and 51.80 µg $HAA_5$ per mg chlorine consumed. The value 19.01 µg $HAA_5$ per mg chlorine consumed obtained here at pH 8 is in line with the value of 18 µg $HAA_9$ per mg chlorine consumed reported by Gang et al. (2002), in their treated water at pH 8. While it was concluded previously that the pH impact was equivocal on HAA yield, it was interesting to note here that β decreased with increasing pH, as it was reported by previous research that HAA formation decreased with increasing pH (Liang and Singer, 2003). Moreover, the formation of $HAA_5$ per mg of chlorine consumed was predominant in the upland water, indicating more active precursors reacting with chlorine than in the lowland water, which explained the greatest concentration of HAAs in the upland water.

Table 6.5 $THM_4$ and $HAA_5$ yield coefficients at three pHs and model coefficient of correlation $R^2$

| | Lowland water | | | Upland water | | |
|---|---|---|---|---|---|---|
| | pH 6 | pH 7 | pH 8 | pH 6 | pH 7 | pH 8 |
| α[a] | 16.24 | 30.54 | 36.84 | 23.36 | 29.75 | 24.41 |
| ($R^2$) | (0.932) | (0.953) | (0.755) | (0.959) | (0.934) | (0.912) |
| β[b] | 26.80 | 26.50 | 19.01 | 51.80 | 45.19 | 42.90 |
| ($R^2$) | (0.969) | (0.950) | (0.954) | (0.911) | (0.953) | (0.865) |

[a] α corresponds to µg $THM_4$/mg $Cl_2$ consumed; [b] β corresponds to µg $HAA_5$/mg $Cl_2$ consumed.

As a summary, it was found here that:

- $THM_4$ and $HAA_5$ were simulated by the chlorine decay model. In general, the models followed approximately the DBP formation trend.
- The pH had a greater impact on α from the lowland water than on α from the upland water.
- The coefficient yield β, which corresponds to µg $HAA_5$ per mg chlorine consumed, decreased with increasing pH.

## 6.4 CHAPTER SUMMARY

In Chapter 5, it was shown that HAAs and THMs were present in all the waters surveyed and therefore, this extensive study on HAAs and THMs was designed to determine the sensitivity of DBP formation to differences in water character and the impact of water treatment parameters. The main results observed here were:

- The greatest pH impact was observed in the formation of THMs in the lowland water. Although THM formation was significantly affected in both waters, $HAA_5$ formation did not exhibit a strong pH effect. When changing the pH, the lowland water behaved as predicted in the reported literature with regard to HAA formation. However the behaviour of the upland water did not follow the same pattern. The differences in the precursor characteristics may account for these observations.
- Addition of bromide to the water leads to a higher percentage of brominated HAAs and THMs. Total $THM_4$ increased, while total $HAA_5$ decreased. The impact on HAAs will vary depending on the number of brominated species measured.
- A reduction in temperature resulted in a major decrease in DBP formation.
- The use of preformed chloramines reduced considerably the formation of HAAs and THMs in UK treated waters.
- Fractions data varied considerably between water sources. The hydrophilic base fraction from the lowland water was the most active towards the formation of HAAs, whereas this was the hydrophobic acid for the upland water. The fraction data obtained previously are based on the level of HAAs formed per mg of carbon. However, each fraction contributed to a different percentage of the mass distribution of NPOC and, therefore, it was necessary to consider the real percentage of the $HAA_9$. Therefore after reconstitution to their real contribution in bulk water, it was concluded that the primary fractions to target for removal were the hydrophilic acid + neutral and the hydrophobic acid for the lowland and the upland water respectively.
- The chlorine decay data could fit a parallel first order reaction model that could be used to predict the formation of HAAs and THMs.
- With the chlorine decay, the first order rate $k_R$ was the fastest at pH 7 for the first part of the reaction, but the pH did not impact the slower part of the reaction. Incorporation of chlorine during the first part of the reaction increased with decreasing pH.

- The impact of pH was greater on α found in the lowland water than α from the upland water. The coefficient yield β, which corresponds to µg $HAA_5$ per mg chlorine consumed, decreased with increasing pH.

As a general conclusion, significant water quality and treatment factors influence the relative distribution and speciation of HAAs and THMs. Although some of the trends followed the literature, some contradict previous findings. This study showed that water utilities should monitor HAAs and THMs throughout their treatment plant, because the formation of HAAs and THMs is highly specific to the water source.

# Chapter 7

## RECOMMENDATIONS FOR WATER UTILITIES

The present study has extended the knowledge of HAAs and other DBPs in treated waters from around the UK. The findings of this study show that levels of HAAs and other DBPs measured in treated waters vary considerably as a function of the geographical location of the water treatment works. The work leads to a number of recommendations based around key questions raised by water companies throughout the duration of the project:

1. *Question*: What is the most appropriate procedure for measuring HAAs?

   *Answer*: The most appropriate method is based on the two stage process of methylation of the HAAs with acidic methanol followed by quantification using GC/ECD. The identified method provides the only approach with a suitable detection limit (1.435 μg/L) in relation to legislative levels. The most common alternative method, which utilises an IC, has a detection level that is not sufficiently sensitive to be useful in practical situations; LOD could not be determined with GC/MS. The GC/ECD method requires around 6 hours of preparation time plus 30 minutes of GC/ECD analysis per sample. For analysis of HAAs with this method consideration must be given to the validation of the method with the specific machine being used in order to determine LOD and peak retention time as this can vary between analytical devices.

2. *Question*: What is the most appropriate procedure for measuring semi-volatile DBPs (if required in future)?

   *Answer*: The most appropriate method is based on a two stage process of LLE followed by quantification using GC/ECD as it is the most rapid and cost effective of the available methods. The identified method has been demonstrated to be suitable for i-THMs, HANs, HKs, HAs and HNMs. The method requires around 2 hours of preparation time plus 30 minutes of GC/ECD analysis per sample. Semi-volatile DBPs are easily degradable, therefore, the quenching

agent should be carefully chosen amongst those known to be inert towards DBPs such as ammonium chloride and ascorbic acid. As for HAAs, individual method validation is required for semi-volatile DBPs when using a new instrument as LOD and peak retention time can vary between analytical devices. The identified method can support more compounds such as other i-DBPs, other HANs, other HKs etc. but would require the use of GC/MS for confirmation if use of a different GC column and/or incorporation of new compounds unknown in the literature.

3. *Question*: What should be included in future DBP surveys?

   *Answer*: Future surveys should focus on $THM_4$ and $HAA_9$ to reflect future regulation. In addition to measuring these DBPs, samples should be analysed for NPOC, $UV_{254}$, and $SUVA_{254}$ and bromide concentrations. The bromide concentration can be used to establish likely speciation based on the threshold limits identified in this work of 75 µg/L for THMs and 100 µg/L for HAAs. In the future when semi-volatile DBPs are included in regulations, further analysis will be required including the iodide levels to compare to threshold limits. This will be equivalent to the bromide case reported above.

   Attempts to find correlations between parameters should be restricted to consistent water sources (e.g. lowland or groundwater) or by process, such as coagulation and pre-ozonation to reduce the uncertainty which is inherent in such work due to the complex nature of the organic make-up.

4. *Question*: Does the fact that a water meets the THM regulatory level mean that it will be likely to meet the future regulations for HAAs?

   *Answer*: NO. A key finding of the current work is a disparity in the correlation between THMs and HAAs such that compliance to the regulation for one group of DBPs does not indicate that the water will also be compliant to the other group of DBPs. As such, waters that have not previously had a problem with THM compliance may be currently unable to meet HAA compliance levels without changing the operating strategy or the need for additional treatment processes.

5. *Question*: How can the formation of DBPs be controlled?

   *Answer*: The work presented has identified a number of parameters in relation to existing treatment works that can be considered when attempting to manage DBP formation:

   *(a)* The switch to preformed monochloramine provides a consistent reduction in DBPs formation within all classes of compounds studied: HAAs, THMs and emerging DBPs, one exception being 1.1-DCP.

   *(b)* The kinetics of the chlorine reactions indicate that reducing the contact time of free chlorine will consistently reduce DBP formation levels.

   *(c)* Alteration of the pH has a significant impact on DBP levels. THMs are consistently reduced in terms of total THMs by operating under more acidic conditions. The impact is less significant and becomes source dependent with respect to HAAs. Based on one sample, a reduction of approximately 15% in total HAAs can be expected in the lowland water when the pH is changed from 6 to 8, whereas this is an increase of approximately 15% in total HAAs in the upland water. As such, pH control of HAAs by switching to alkaline conditions is only suitable for lowland water.

   *(d)* Temperature has a consistent impact with reduced DBPs under lower temperature conditions. Whilst temperature is not a control variable in practice it should be recognised that, with all other factors considered, maximum DBPs will form in the summer. In practice this is complicated as load and character of the organics change with season complicating the impact of this parameter.

   *(e)* Removal of specific precursors will reduce DBPs significantly. Whilst individual precursor molecules are unknown, the work has identified key organic fractions to target for different water sources. The specific fractions are the hydrophilic acid + neutral fraction for lowland water and the hydrophobic acid fraction for upland water. Focussing treatment optimisation and improvements on these fractions should maximise the

impact of any changes in terms of reduction of DBPs and should guide future technology selection.

# Chapter 8

## CONCLUSIONS

This project has extended the knowledge of DBP-FP from UK treated waters. Specifically the work detailed in the thesis has identified the most suitable method for the quantification of HAAs, and also developed an analytical method for the determination of semi-volatile DBPs. Application of these methods to a survey of 11 different waters from around the UK indentified the complex interaction between the variation in water quality characteristics, treatment flow sheet and the quantity and speciation of the DBPs formed. Results presented in the thesis have voluntary been quantified in µg/L in order to compare directly with the regulations set-up and to come. However, it must be considered that adjusting these data to molar concentrations may have an impact on the trends reported here.

Analysis of the resulted presented in this thesis leads to the following overall conclusions:

1. The monitoring of HAAs and other DBPs can be achieved with reliable and reproducible methods. The most suitable analytical method for the measurement of nine HAAs in UK treated water is the methylation of the HAAs followed by quantification with GC/ECD, with a detection limits for the sum of the nine HAAs being 1.435 µg/L. Alternative methods such as the IC are not suitable as their detection limits are too high; LODs for IC are 2.6 to 31.9 µg/L for individual HAA. The most rapid and cost-effective method for the monitoring of 16 semi-volatile DBPs is LLE followed by quantification using GC/ECD, with a detection limit for the sum of the 16 compounds being 0.907 µg/L. As a general overview, the best device for the analysis of DBPs in treated waters is the GC/ECD. In general, the use of FP test was shown to be a very useful mean of understanding the formation of DBPs. However, the use of FP test was found unsuitable for the quantification of i-THMs as the chlorine, used in excess, is likely to limit their formation.

2. HAAs and semi-volatile DBPs including THMs, i-THMs, HANs, HKs, HAs and HNMs were detected in UK treated waters. The 11 surveyed waters have the potential to form a maximum of 68 µg/L for $HAA_9$, 66 µg/L for $THM_4$, 0.73 µg/L for i-THMs, 5.5 µg/L for HANs, 3.9 µg/L for HKs, 9.5 µg/L for HAs and 3.4 µg/L for HNMs. Improving the control of HAAs and other DBPs can be achieved by using monochloramine instead of free chlorine, as it has been found that, in general, a decrease in DBP concentrations has been observed when shifting from chlorine to monochloramine, the one exception being 1,1-DCP. The prevalent classes of DBPs were HAAs and THMs; HAs were found to be the third major group. In general, the concentrations of THMs correlated well with HAAs, and in particular the levels of TCM were similar to the levels of TCAA supporting the hypothesis that they share similar precursor material. Analysis of the correlation revealed that, in general, the regulatory limit of 100 µg/L for the $THM_4$ would fail a regulation of 80 µg/L for the nine HAAs.

3. Modelling of the formation of HAAs and THMs using a parallel first order reaction model, fitted to the chlorine decay data provided a good method of prediction of the DBP formation levels. Thus, the rate of DBP formation is characterised by a general trend of an initial rapid reaction during the first few hours, followed by a steady rate of increase over the 168 hours of contact time with chlorine.

4. The work outlined in the thesis identified a number of parameters which have particular relevance when considering the formation of HAAs and THMs in treated waters and it can be concluded that these factors should always be considered when investigating or measuring DBPs:

    - The data identified threshold bromide level beyond which the speciation of HAAs shifts toward predominantly brominated species. The threshold levels were identified as 100 µg/L for HAAs and 75 µg/L For THMs.

    - Management of the balance of THM and HAA is, in part, possible through pH control as THM formation is significantly affected by the pH whereas, $HAA_5$ formation is less strongly linked. The impact in

relation to HAAs is further complicated by a switch in the impact of pH by water sources. This is illustrated by a decrease of 15% in HAAs for a lowland water and an increase of 14% as the pH switches from slightly acidic to slightly alkaline.

- Another important parameter affecting HAAs is the precursor make-up. The use of bulk water characteristics, such as NPOC or SUVA, as surrogates does not provide suitable means of controlling DBPs. This is illustrated in its simplest form by the fact that two waters with similar water characteristics can form different level of DBPs. Instead characterisation by means of non specific ion exchange fractionation indentifies the key group of compounds to target for each source water type. Specifically, from the data presented it can be concluded that the primary fractions to target for removal in order to minimise DBP formation are the hydrophilic acid + neutral for lowland water and the hydrophobic acid fraction for upland water.
- Temperature has a consistent impact with a decreasing DBP formation in lower temperatures and thus seasonal consideration will always be important when considering strategies to meet legislative compliance levels but must be viewed in combination with the other factors above.

# Chapter 9

## FURTHER WORK

The results of the present work highlight the complexity of the formation of HAAs and other DBPs in UK treated waters and show that we are still far from a full understanding. Furthermore, all results were obtained from controlled laboratory scaled experiments. Further research should apply the laboratory findings to drinking waters from the distribution systems, and focus on:

- *Monitoring semi-volatile DBPs:* The results found here showed that all the waters studied had not only HAAs and THMs, but also i-THMs, HANs, HKs, HAs and HNMs. This is the first time these compounds have been detected in UK treated waters and, therefore, more work should be done to investigate the real potential of drinking water to form these DBPs. The work should use samples from different points of a distribution system to determine levels and stability of these compounds. Seasonal variation could also be investigated in order to determine the impact of NOM variation on the level of DBPs.
- *Expand the number of DBPs monitored:* Whereas 25 compounds have been measured in the present study, about 100 DBPs are currently studied in the US for their moderate occurrence levels and their potential toxicity. Therefore, further work should focus on targeting new compounds, such as the iodo-acids, the halofuranones (MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone] and brominated MX DBPs), N-nitrosodimethylamine (NDMA) and other nitrosamines, etc. and set-up analytical methods for their measurement.
- *Set-up and monitor dissolved organic nitrogen (DON) levels, removal and reactivity with chlorine:* There is evidence that the DON present in NOM acts as precursors to nitrogen-containing DBPs. This is important, because N-DBPs have been reported to be more toxic than chlorinated or brominated DBPs.

- *Set-up and monitor total organic halogen (TOX), with its halogen-specific fraction: total organic chlorine (TOCl), total organic bromine (TOBr) and total organic iodine (TOI):* TOX screening can be used to quantify the chlorinated, brominated and iodinated organic compounds in drinking waters. By determining TOX and the known DBP concentration, it would then be possible to estimate the percentage of unknown DBPs in UK drinking waters.
- *Understanding the pathways and links between DBPs*: Further research should focus on progressive degradation of one species into a new species. For example, this work could be carried out by spiking a known amount of TCM into pure water and by adding excess chlorine for a determined contact time. At the end of the incubation period, the sample could be analysed by GC/ECD for analysis of DBPs. In this way, the DBP degradation or transformation could be easily determined, as well as the link between species.
- *CT values when using chloramines as a secondary disinfectant*: A long pre-chlorination time results in higher concentration of DBPs. Therefore, by optimising the CT values, a possible decrease of DBPs could be expected.

# Chapter 10

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