

# **Minimisation of regulated and unregulated disinfection by-products in drinking water**

By **Chrysoula Sfynia**

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Department of Civil and Environmental Engineering

Imperial College London

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## Abstract

This research, involving a collaboration between Imperial College London and Anglian Water, had the overall aim to understand the occurrence and fate of a wide range of disinfection by-products (DBPs) during drinking water distribution and to establish operational strategies to simultaneously control them in water supply systems. Therefore, the research is essentially centred on two main issues: i) improving our understanding of the impact of water quality and operational parameters on regulated and unregulated DBPs in water distribution networks, and ii) the validation of a prediction tool to proactively design and adapt operational practices to minimise DBPs.

The research explored these issues through a series of experiments focused on the analysis of 29 DBPs upon chlorination and chloramination, under various water ages and water quality conditions, by sampling from four locations in four full-scale distribution systems in four sampling rounds and simultaneously running Simulated Distribution System (SDS) tests. This resulted in one of the most comprehensive databases of the occurrence and behaviour in distribution systems of regulated trihalomethanes (THMs), the likely-to-be-soon-regulated-in-the-UK haloacetic acids (HAAs), as well as unregulated haloacetonitriles (HANs) and haloacetamides (HAcAms) of potential health significance, and their individual species. For the first time, SDS tests were shown to be able to successfully predict the levels and speciation of HANs and HAcAms in chlorinated and chloraminated systems, by direct comparison with actual distribution water samples. The configuration of SDS tests addressed the spatial and temporal variation of the selected DBPs, indicating that THM concentrations significantly increase with water age (on average by ~54% between water ages of 6-106 h) and present high seasonal dependence, together with HAAs. The latter, HANs, and HAcAms concentrations had fluctuations that resulted in less pronounced overall increases, with the two N-DBPs relatively unaffected by water temperature. To explore the impact of disinfectant alteration in distribution, free chlorine and chloramination were applied in the same real water samples in SDS tests. This showed that the implementation of chloramination minimises the formation not only of THMs and HAAs, but also HANs and HAcAms, though it shifts speciation towards more brominated HAAs, HANs and HAcAms species. Through this research, SDS tests can be recommended to water utilities to both estimate the concentrations of DBPs (those included in this study) in their supply systems and assess the effect of potential DBP minimisation strategies.

The interesting behavioural patterns of HAcAms in distribution systems raised questions concerning their formation mechanisms and determining factors. Therefore, a laboratory study was conducted whereby chlorination and chloramination were applied to six model amide compounds to investigate their relative contributions as N-DBPs precursors, under a range of water quality conditions (pH, bromide dose, water age). The findings of this study suggest that the N-oxidation of amide structures, more evident in aromatic moieties, is a potential mechanism for HAcAms formation, which occurs completely separately from HAN hydrolysis. This suggests that if precursor removal is to be used as a treatment strategy for minimising HAcAms and HANs, the success in minimising these groups of N-DBPs may differ based on the relative success in removing their independent precursors.

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## Glossary

|                                |                                                                                |
|--------------------------------|--------------------------------------------------------------------------------|
| AWWA                           | American Water Works Association                                               |
| BCAN                           | Bromochloroacetonitrile                                                        |
| BCNM                           | Bromochloronitromethane                                                        |
| BNM                            | Bromonitromethane                                                              |
| Br                             | Bromide                                                                        |
| BIF                            | Bromine incorporation factor                                                   |
| CAN                            | Chloroacetonitrile                                                             |
| C-DBPs                         | Chlorinated disinfection by-products                                           |
| Cl <sub>2</sub>                | Chlorine                                                                       |
| CNM                            | Chloronitromethane                                                             |
| CP                             | Chloropicrin                                                                   |
| DBAcAm                         | 2,2-Dibromoacetamide                                                           |
| DBAN                           | Dibromoacetonitrile                                                            |
| DBCAN                          | Dibromochloroacetonitrile                                                      |
| DBCNM                          | Dibromochloronitromethane                                                      |
| DBNM                           | Dibromonitromethane                                                            |
| DBP                            | Disinfection by-product                                                        |
| DCAcAm                         | 2,2-Dichloroacetamide                                                          |
| DCAN                           | Dichloroacetonitrile                                                           |
| DCNM                           | Dichloronitromethane                                                           |
| DHAN                           | Dihaloacetonitrile                                                             |
| DON                            | Dissolved organic nitrogen                                                     |
| DPD-FAS                        | N, N-diethyl-p-phenylenediamine- ferrous ammonium sulphate                     |
| ECD                            | Electron capture detection                                                     |
| GC                             | Gas chromatography                                                             |
| GW                             | Groundwater                                                                    |
| H <sub>2</sub> SO <sub>4</sub> | Sulfuric acid                                                                  |
| HAA <sub>9</sub>               | The nine species of haloacetic acids                                           |
| HAAs                           | Haloacetic acids                                                               |
| HAcAms                         | Haloacetamides                                                                 |
| HALs                           | Haloacetaldehydes                                                              |
| HANs                           | Haloacetonitriles                                                              |
| HKs                            | Haloketones                                                                    |
| HNMs                           | Halonitromethanes                                                              |
| Log K <sub>ow</sub>            | Ratio of the concentration of a chemical in n-octanol and water at equilibrium |
| MBAN                           | Monobromoacetonitrile                                                          |
| MDL                            | Method detection limit                                                         |
| MS                             | Mass spectrometry                                                              |
| MTBE                           | Methyl tertiary-butyl ether                                                    |
| N-DBP                          | Nitrogenous disinfection by-products                                           |
| NDMA                           | N-nitrosodimethylamine                                                         |
| NH <sub>2</sub> Cl             | Monochloramine                                                                 |
| NO <sub>2</sub>                | Nitrite                                                                        |
| NO <sub>3</sub>                | Nitrate                                                                        |

|                   |                                                                |
|-------------------|----------------------------------------------------------------|
| NOM               | Natural organic matter                                         |
| O <sub>3</sub>    | Ozone                                                          |
| PBT               | Polybutylene Terephthalate                                     |
| pH                | Negative logarithm (base 10) of the hydrogen ion concentration |
| PPE               | Personal Protection Equipment                                  |
| PR                | Price review                                                   |
| PTFE              | Polytetrafluoroethylene (Teflon)                               |
| SUVA              | Specific ultraviolet absorbance                                |
| TCAcAm            | 2,2,2-Trichloroacetamide                                       |
| TCAN              | Trichloroacetonitrile                                          |
| THM <sub>4</sub>  | The four species of trihalomethanes                            |
| THMs              | Trihalomethanes                                                |
| TOC               | Total organic carbon                                           |
| TOX               | Total organic halides                                          |
| TXAA              | Trihaloacetic acid                                             |
| UKWIR             | United Kingdom Water Industry Research                         |
| UV                | Ultraviolet                                                    |
| UV <sub>254</sub> | UV absorbance at 254 nm                                        |

## Chapter 1. Introduction

Innovation in engineering occurs not only via the implementation of new technologies, but also via the optimisation of existing processes to accomplish new goals. This is particularly important in the water industry, since water treatment infrastructure is provisioned to deliver high quality potable water for several decades, however amid its lifetime, must also have the capacity to adapt to new challenges as they arise, such as changes of raw water quality or the emergence of new contaminants. One of the current water quality challenges faced by water utilities in the UK is the need to review their water treatment or disinfection practices, or introduce new ones, to minimise the formation of disinfection by-products. The Drinking Water Inspectorate in 2012 stated that for PR14 (price review) water companies must show that they *‘design, operate and maintain the disinfection process so as to keep disinfection by-products as low as possible without compromising the effectiveness of the disinfection’* (DWI 2012). Following that, in January 2014, the United Kingdom Water Industry Research (UKWIR) published a report entitled ‘DBP Risk assessment: DBPs of concerns’, which identified the most significant DBPs under UK conditions (UKWIR 2014).

Disinfection of drinking water in treatment and distribution aims to safeguard consumers against the occurrence of waterborne diseases related to microbial contaminants and has been characterised as ‘one of the most significant public health advancements’ of the last century (CDC 2000; Richardson et al. 2007). The use of oxidants, such as chlorine, chloramines and ozone to disinfect drinking water has virtually eliminated water-borne diseases such as typhoid, cholera and dysentery in developed countries. However, research has shown that these disinfectants interact to varying degrees with natural organic matter (NOM), inorganic compounds and anthropogenic constituents present in drinking water supplies to form *disinfection by-products* (DBPs).

Disinfection by-products have been a significant area of investigation since the mid-1970s following two publications (Rook 1974; Bellar et al. 1974) that reported the relation between chloroform formation and the reactions of natural organic matter (NOM) and chlorine. To-date, literature refers to more than 700 DBPs from the main disinfection methods currently implemented, as well as their combinations (Richardson 1998; UKWIR, 2014). Nevertheless, the percentage of the identified DBPs is small (~37%) in comparison with the mass of the unknown organic halogens in water that has not been identified (~63%) (Richardson 2002; Krasner et al. 2006), as demonstrated in Figure 1.1. From this identified amount of

DBPs, an even smaller percentage has been quantified in drinking waters and distribution systems (Weinberg et al. 2002).

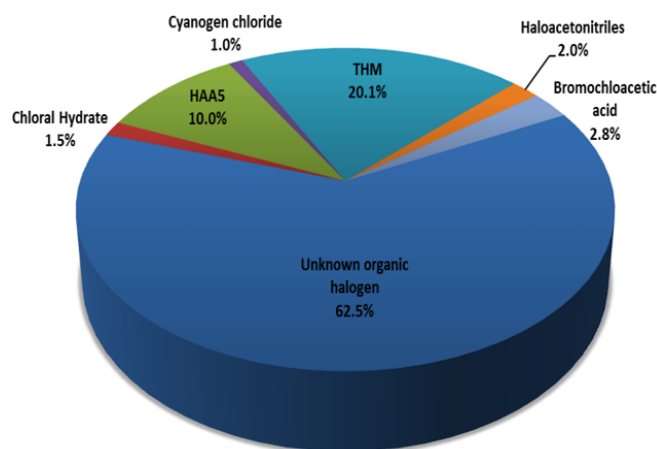


**Figure 1.1:** The percentage of total organic halogen (TOX) mass that has been identified in literature to-date (adapted from Richardson 2002; Krasner et al. 2006).

Research on the field is fast-evolving as several DBPs are known or suspected to pose certain risks to public health, namely increased potential risk of urinary bladder cancer, over long term exposure (Richardson et al. 2007; Villanueva et al. 2007) or adverse reproductive outcomes over shorter time exposure (Nieuwenhuijsen et al. 2009; Grellier et al. 2010). Populations that consume drinking water from public water supply networks are regularly exposed to DBPs through everyday water consumption via ingestion, inhalation and dermal contact (Chowdhury et al. 2009). Therefore, several environmental organizations and countries have published regulations and guidelines to control the formation of some known DBPs in drinking water in order to protect public health (EU 1998; US EPA 2006; Health Canada 2009; Japanese Ministry of Health 2010; NHMRC, NRMMC 2011; WHO 2011b).

One broad group of unregulated DBPs, in particular, for which further knowledge on occurrence and formation mechanisms is needed are the nitrogen-containing DBPs (N-DBPs), such as haloacetamides and haloacetonitriles, which are suspected to be more toxic than the non-nitrogenous regulated counterparts (Richardson et al. 2007; Plewa et al. 2008). Furthermore, much of the published research has focused on regulated and unregulated DBP formation within water treatment works, yet there is only sparse information about the typical concentrations of many of these compounds in tap water as well as the impact of distribution system parameters on their formation or their ultimate fate in distribution systems, i.e. after the water leaves the water treatment works. Indeed, DBPs are known to exhibit significant *spatial* and

*temporal* variability due to raw water quality fluctuations (TOC, NOM constituents, bromide level) and/or due to the conditions in the distribution networks (disinfectant residuals, pH and water temperature). The levels of the most abundant DBP class, THMs, are known to increase with increasing water age in distribution, whereas some HAAs have been reported to chemically and biologically degrade (Koch et al. 1991; Singer et al. 2002; Baribeau et al. 2006). As far as the unregulated DBPs are concerned, HANs and HAcAms, the knowledge on their occurrence and fate in distribution networks is very limited. All of the above have been the drivers for this research project with the aim to contribute to new knowledge in the field of DBP minimisation in water distribution systems.

The potential of DBPs to impact upon a variety of health outcomes has highlighted the industry challenge of achieving microbiological water quality compensation while minimizing the risks associated with exposure to DBPs. Even though Anglian Water has always attempted to achieve the appropriate balance of disinfecting potable water whilst maintaining compliance to the regulatory DBP limits within their systems, they are continuing to investigate ways to keep DBP concentrations '*as low as possible*'. This was the motivation for Anglian Water to fund this research, with the aim to understand the occurrence and fate of regulated and unregulated DBPs in their systems and to establish operational strategies to simultaneously minimise them during drinking water treatment and distribution. It was decided that this research should exclude N-nitrosodimethylamine (NDMA) and iodinated DBPs, since the collaborating water utility already had separate means of accessing data for those DBPs and including them would have considerably increased the cost and practical difficulty within the time available, given the need for separate sampling and analytical protocols.

It should always be emphasised that the benefits provided by drinking water disinfection outweigh the potential health risks associated with DBPs, and DBP minimisation strategies therefore should never impact on the effectiveness of disinfection.

## 1.1 Thesis Outline

The research thesis consists of seven main chapters for Introduction, Literature review, Materials and Methods, followed by the Results that analyse all the experimental results and summarise the main findings. The penultimate chapter is the Discussion chapter that assimilates the key findings from the various aspects of this PhD research, concluding with the closing chapter of Conclusions which summarises the contributions to knowledge of this research and recommendations for water utilities on devising operational strategies to minimise the regulated and unregulated DBPs in water distribution systems. After the final chapter, the literature references as well appendices can be found, that include the complete database on the target DBPs from the actual and simulated distribution systems and supplementary information.

During the duration of the research project two peer-reviewed conference proceeding papers were published:

Sfynia Chrysoula, Tom Bond, Rakesh Kanda, and Michael R Templeton. 2017. '*Predicting the formation of haloacetonitriles and haloacetamides by simulated distribution system tests*'. Procedia Engineering, Volume 186, XVIII International Conference on Water Distribution Systems, WDSA2016, pp. 186-192.

Sfynia Chrysoula, Tom Bond, Rakesh Kanda, and Michael R Templeton. 2016. '*Nitrogenous Disinfection By-Product Formation from the Chlorination and Chloramination of Amides*'. In American Water Works Association - Water Quality Technology Conference and Exposition 2016. Indianapolis, IN, USA.

With the completion of this research, two journal publications are in preparation for submission in early 2018 entitled:

*Predicting the formation of regulated and unregulated DBPs using simulated distribution system tests* (target journal: Water Research).

*The formation of haloacetamides and other DBPs from the chlorination and chloramination of amides* (target journal: Water Research).

## Chapter 2. Background and Literature Review

Even though disinfection practices had been implemented in potable water supply systems for several decades, it was not until the early 1970s when scientists reported for the first time the generation of residual chemical hazards. Disinfection by-products in drinking water have been a major research subject over the past 40 years, with ongoing and fast-evolving activity internationally. Considerable research has addressed the formation and control of DBPs, particularly THMs, via *in situ* sampling, controlled laboratory conditions and modelling, since these compounds are currently regulated for being of health significance. However, we now know of hundreds of by-products which regularly occur in treated drinking waters, including haloacetic acids, haloacetonitriles, haloacetamides, halo ketones, and nitrosamines (Krasner et al., 2006; Bull et al., 2007; Richardson et al., 2007; Templeton et al., 2010 & 2012). Some of these emerging DBP groups may be more genotoxic and cytotoxic than the regulated DBPs (Bull et al., 2007; Pals et al., 2011), yet there is only sparse information about the mechanisms by which they are formed during water treatment/distribution, their behaviour in distribution systems, the typical concentrations in tap water, and their most important precursors and formation mechanisms.

A large number of research papers have been dedicated to the formation of various DBPs and the means to control them, including enhanced precursors removal. However, fewer studies have investigated the occurrence, speciation and behaviour of DBPs in distribution systems. This background chapter commences with a brief review of the DBPs, addressed in this project, and their reported occurrence in distribution systems. A summary of available information to date with regards to the key factors that influence DBP formation, behaviour and stability in distribution systems is then presented, followed by the currently researched strategies for DBP minimisation in drinking water. Finally, a brief description of the implementation of the simulated distribution system (SDS) tests in previous studies is presented at the end of the literature review.

## 2.1 Definition and occurrence of regulated and unregulated DBPs in distribution

### 2.1.1 Trihalomethanes (THMs)

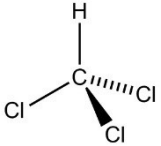
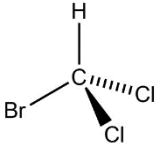
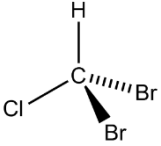
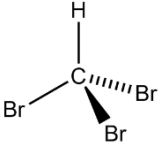
Trihalomethanes are halogenated forms of methane which are susceptible to volatilisation and formation through disinfection of natural water. THMs are reported as being the most predominant disinfection by-products in drinking water by mass, accounting for approximately 20% of the identified halogens (Krasner et al. 2006) and the most extensively studied DBP group. The four chlorinated and brominated THM species are chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), and bromoform ( $\text{CHBr}_3$ ), organised in *Table 2.1*. These substances can be generated from various organic precursors found in natural water matrices, including humic and/or fulvic composites (Reckhow et al. 1990; Larson and Weber 1994), activated aromatic (e.g. phenols) and aliphatic moieties (e.g.  $\beta$ -dicarbonyl, amino acid and carbohydrate precursors) (Norwood et al. 1980; Hureiki et al. 1994; Dickenson et al. 2008; Bond et al. 2012), and ketones. In addition, there are suggested reaction pathways through which THM may also form from a complex sequence of decarboxylation and hydrolysis reactions of other DBPs, linked with alteration of water quality conditions (Larson and Rockwell 1979; Boyce and Hornig 1983).

In the US, a considerable number of surveys have been conducted to evaluate the occurrence of THMs in drinking water, both prior to distribution and in the networks (Krasner et al. 1989; Bull et al. 2001; Weinberg et al. 2002). According to the Information Collection Rule database involving 500 treatment works, the THMs present significant topographic variation, with median and 90<sup>th</sup> percentile values of 33 and 78  $\mu\text{g/L}$ , with the lowest values reported in cold regions, Pacific northwest and Alaska, and highest in inland south regions (McGuire et al. 2002). In Europe, THMs are regularly monitored by water utilities in finished waters, since these are the only DBPs regulated by the European Union's Drinking Water Directive, with total concentrations required to be below 100  $\mu\text{g/L}$  (European Union 1998). A three-year occurrence survey was recently published by Krasner et al. (2016), where collaborative groups collected DBP values from 13 chlorinated water works, including THMs, in Italy, France, Greece, Lithuania, Spain, United Kingdom. Total THM concentrations from each system ranged from 0.2 to 197  $\mu\text{g/L}$  (10<sup>th</sup> to 90<sup>th</sup> percentile), with the highest median value of 77  $\mu\text{g/L}$  reported in Catalonia (Spain), followed by 44  $\mu\text{g/L}$  in Rennes (France) and 30  $\mu\text{g/L}$  in Bradford (United Kingdom). Brominated species of THMs were significantly higher in coastal regions, due to salination of surface and groundwater water reservoirs. In the UK, total THMs occur in typical concentrations of 25-50  $\mu\text{g/L}$  (UKWIR 2014), with dibromochloromethane, followed by bromoform, being the dominant species in ground and lowland surface

waters (Whitaker et al. 2003). One of the most important limitations for English water utilities to form a comprehensive framework in controlling their THM levels is the fact that routine monitoring for regulatory purposes is being conducted in a random selection from all the downstream locations. Therefore, even though THM levels are monitored and recorded, the available information is inconsistent in terms of spatial and temporal variations.

Several researchers have reported increasing THM levels in relation with increasing water age and distance from the water treatment plant (Koch et al. 1991; LeBel et al. 1997; Williams et al. 1997; Baribeau et al. 2006). However, these increases are observed to be substantially lower in chloraminated than in chlorinated distribution systems (Obolensky and Frey 2002). In a study conducted by Vasconcelos et al. (1997), those total THMs that increased with water age were linked with a significant decrease in chlorine residual, due to organic content consumption, however Obolensky and Frey 2002 argued that the increases in chloraminated systems with water age were relatively minimal. The four species of trihalomethanes, together with their molecular weight and structure are summarised in Table 2.1, below.

**Table 2.1:** Characteristics of trihalomethanes (THMs) monitored.

| THMs species         |                          | Molecular weight [g/mol] | Chemical structures                                                                   |
|----------------------|--------------------------|--------------------------|---------------------------------------------------------------------------------------|
| Chloroform           | $\text{CHCl}_3$          | 119.37                   |  |
| Bromodichloromethane | $\text{CHBrCl}_2$        | 163.80                   |  |
| Dibromochloromethane | $\text{CHBr}_2\text{Cl}$ | 208.28                   |  |
| Bromoform            | $\text{CHBr}_3$          | 252.73                   |  |

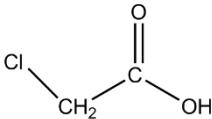
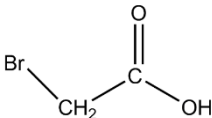
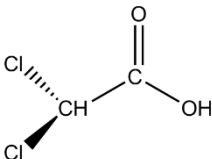
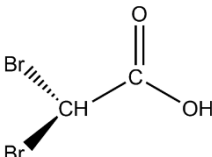
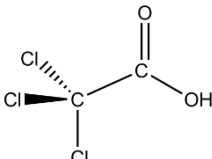
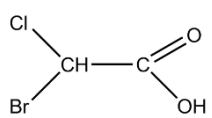
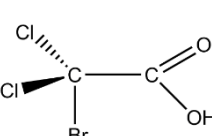
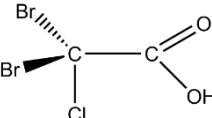
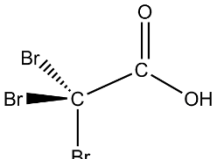
### 2.1.2 Haloacetic Acids (HAAs)

Haloacetic acids are halogenated forms of carboxylic acids, characterised as non-volatile and are the second most abundant class of DBPs by mass formed during disinfection, even though sometime found at similar or even higher yields than THMs (Baribeau et al. 2006). The precursors for HAA are humic substances, and specifically the hydrophobic fraction, as well as aromatic substances (i.e. resorcinol), malonic, amino, other carboxylic acids and algae (Norwood et al. 1980; Hureiki et al. 1994; Dickenson et al. 2008; Bond et al. 2012). There are nine chlorine- and bromine-containing haloacetic acids, presented in *Table 2.2*, of which only the first five are currently regulated in the US (US Environmental Protection Agency 2006). However, analytical methods have been developed to include all nine HAAs and it is suggested to water utilities to extend their monitoring, since future regulatory activity will be possibly directed at all nine HAAs. Also, the World Health Organisation has published guideline values for DCAA and TCAA at 50 and 200 µg/L (WHO 2011b). In the UK, the concentration of haloacetic acids is not currently a regulated parameter, however research papers have highlighted their widespread occurrence in drinking water (Malliarou et al. 2005; Goslan et al. 2009; Zhang et al. 2011) and reports to the European commission have recommended the future inclusion of nine HAAs in the EU Drinking Water Directive, with a maximum level of 80 µg/L (DWI 2002; Defra 2005).

In the UK and Europe there is relatively little information on the occurrence of HAAs in treated drinking water and distribution systems. More specifically, Malliarou et al. (2005) analysed six HAAs species from treatment works applying chlorine and reported total mean values ranging from 35-95 µg/L in three different regions of England, with the most abundant species being those of DCAA and TCAA. Following this, a nationwide occurrence survey (20 water treatment plants) conducted by Parsons and Goslan (2009) for DWI, reported total HAAs in distribution systems ranging between 8-74.8 µg/L (*median 20.8*). This study included all nine HAAs from various source waters (lowland, upland and groundwater sources) and observed concentration increase in most of the distribution networks observed, except in those that were using chloramines. A different study that included 7 water treatment plants from Scotland reported generally higher total HAA concentrations, ranging between 11-134 µg/L, and concluded that HAA were significantly higher in treatment works applying chlorine in comparison with those applying chloramines (Goslan et al. 2009). However, a survey conducted by Graham et al. (2009) that also included a groundwater source reported even lower total HAA levels, with median and maximum HAA levels in lowland surface waters being 11.9 µg/L and 20 µg/L, respectively.

HAAs levels have been reported to fluctuate within the water networks and total concentrations have been observed to both increase and decrease in chlorinated distribution systems with water age (Baribeau et al. 2006). When HAA have been measured in full-scale chlorinated distribution systems, Koch et al. (1991), Singer et al. (2002), Obolensky and Frey (2002) reported higher yields in downstream location characterised by the maximum water age than those with the lowest water age, with di- and tri-HAAs exhibiting considerable increases. Several other researchers, though, observed the opposite pattern with HAAs reduction as a high as 50% between the furthest and closest downstream location (LeBel et al. 1997; Williams et al. 1997; Chen and Weisel 1998). The increases have been related to continuous reactions of chlorine and NOM, and HAcAms degradation, whereas decreases have been hypothesised to be related to biodegradation and chemical decomposition (Reckhow et al. 2001; Hozalski et al. 2001; Tang et al. 2013). In addition, Tri-HAAs decrease has been associated with the formation of THMs, via hydrolysis, while these two classes are suspected of sharing the same precursors (Stevens et al. 1989; Reckhow et al. 1990). Furthermore, while mono- and di- HAAs species are relatively susceptible to biodegradation, tri-HAAs are more recalcitrant to biological reduction (Zhou and Xie 2002) but more receptive to chemical dehalogenation than the other two groups (Hozalski et al. 2008; Tang et al. 2013; Wang et al. 2013). The order of biodegradability has been reported as mono-HAA > di-HAA > tri-HAA with the corresponding bromine-containing species being easier degraded than the chlorine-containing (Zhou and Xie 2002). Concerning the pattern in literature on chloraminated systems, there is limited information and it argues that HAAs are relatively constant with regards to water age, even though in downstream locations of > 120 hours significant decreases (23-85%) have been observed (Baribeau et al. 2006).

**Table 2.2:** Characteristics of haloacetic acids (HAAs) monitored.

| HAAs species             |       | Molecular weight [g/mol] | Chemical structures                                                                   |
|--------------------------|-------|--------------------------|---------------------------------------------------------------------------------------|
| Monochloroacetic acid    | MCAA  | 94.49                    |    |
| Monobromoacetic acid     | MBAA  | 138.95                   |    |
| Dichloroacetic acid      | DCAA  | 128.94                   |    |
| Dibromoacetic acid       | DBAA  | 217.84                   |   |
| Trichloroacetic acid     | TCAA  | 163.38                   |  |
| Bromochloroacetic acid   | BCAA  | 173.39                   |  |
| Bromodichloroacetic acid | BDCAA | 207.84                   |  |
| Dibromochloroacetic acid | DBCAA | 252.28                   |  |
| Tribromoacetic acid      | TBAA  | 296.74                   |  |

### 2.1.3 Haloacetonitriles (HANs)

Haloacetonitriles (HANs) belong in the broad group of nitrogenous disinfection by-products (N-DBPs), which have received increased research attention during recent years (Yang et al. 2007; Krasner 2009; Bond et al. 2011; Nihemaiti et al. 2016; Sfynia et al. 2016). Even though this nitrogen containing DBP group occurs at lower concentrations in drinking water than THMs and HAAs, they may pose increased health risks due to their suspected higher genotoxicity and cytotoxicity (Richardson et al. 2007; Plewa et al. 2008). There are nine chlorine- and bromine-containing haloacetonitriles presented in *Table 2.3*, of which none is currently regulated anywhere in the world in drinking water. Nonetheless, the WHO has recommended guideline values for two HAN species, DBAN and DCAN at 70 µg/L and 20 µg/L, respectively (WHO 2011b).

HANs are reported to represent approximately 10% (*by mass*) of total levels of THMs and HAAs in distribution systems, with median concentration of 3 µg/L and maximum of 14 µg/L, as identified in a US N-DBP occurrence survey (Oliver 1983; Krasner et al. 2006; Mitch et al. 2009). Oliver (1983) identified HANs (Di-HANs) for the first time in chlorinated water samples, and since then they have been incorporated in several occurrence surveys (Weinberg et al. 2002; McGuire et al. 2002; Mitch et al. 2009; Bond et al. 2015). A literature survey by Templeton et al. (2010) provided useful information on the key factors affecting HANs formation, as was believed to be the case up until then. The main risk factors identified during the above survey were the amount of DON amount, bromide, the acidic pH and chloramination. Even though chloramination has shown to encourage the formation of cyanogen chloride (Krasner et al. 1989) and NDMA (Valentine and Barrett 2006), which also belongs in the N-DBP group, and has been suspected to promote HAN formation via inorganic nitrogen incorporation, the relative effect of chloramines in the formation of HANs is still unknown (Bond et al. 2014). Indeed, in the US nationwide survey, HAN levels have been reported to be elevated in systems that perform chloramination in comparison to those with free chlorine (Weinberg et al. 2002), however the opposite or minimal concentration differences have been observed in the subsequent studies, both in the US and UK (Goslan et al. 2009; Krasner et al. 2012; Templeton et al. 2012). A survey in water samples from Scotland reported that the median levels of four HANs species were 1.7 µg/L during chlorination and 1.3 µg/L during chloramination (Goslan et al. 2009). On the contrary, Lee et al. (2007) found that DCAN generation was on average 5 times greater during chloramination than in chlorination, in controlled laboratory experiments using 17 NOM fractions. Despite the recent upsurge in HAN research (Krasner et al. 2006; Mitch et al.

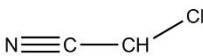
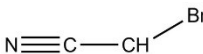
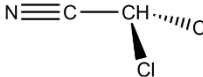
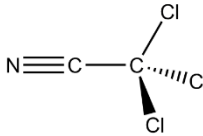
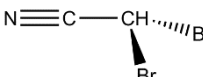
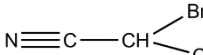
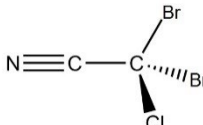
2009; Bond et al. 2011, 2015), there is still sparse information concerning their occurrence and fate in distribution systems.

From a practical standpoint an important knowledge gap concerning the occurrence of HANs in distribution systems is their relationship with water age in both chlorinated and chloraminated systems. Templeton et al. (2012) linked total HAN concentrations with distance from the water treatment plant and found that median concentrations slightly increased between the closest and furthest downstream location, from 2.6 µg/L to 2.8 µg/L. In addition, Koch et al. (1991) has observed that HAN levels between the treatment plant the final downstream location, either remained similar (approx. 7 µg/L) or slightly decreased, with multiple intermediate fluctuations over a period of 100 hours. Nevertheless, distance does not account for the systems design and demand, and the way of estimating the length between the treatment plant and downstream locations may differ among the studies (Berry 1996); straight line or pipe length.

Furthermore, a significant amount of research has focused in the investigation of potential HAN precursors by performing controlled laboratory tests with model compounds that are ubiquitous in natural water. Nitrogen-containing organic compounds (e.g. amino acids, amines, lignin phenols, pyrroles, pyrimidines) as well as waters with enriched organic content (e.g. algal or wastewater impacted sources), have been associated with the generation of HANs (Lee et al. 2007; Dotson et al. 2009; Bond et al. 2012; Bond et al. 2014; Hua et al. 2014). Nevertheless, previous studies indicated that HANs can also be formed with non-nitrogenous precursors (e.g. aldehydes), via inorganic nitrogen incorporation (Kimura et al. 2013; Nihemaiti et al. 2016).

To date, there are two proposed pathways to describe the formation of HANs; the decarboxylation and the aldehyde pathway. The first, the decarboxylation pathway, is characterised by a rapid oxidation of the α-amine group of amino acids to form a nitrile, followed by a hydrolysis to release HANs and H<sub>2</sub>CO<sub>3</sub> (Trehay et al. 1986). The latter, the aldehyde pathway, involves the incorporation of the inorganic nitrogen, found in chloramines, into the aldehydes to generate nitriles (Kimura et al. 2013).

**Table 2.3:** Characteristics of haloacetonitriles (HANs) monitored.

| HANs species              |       | Molecular weight [g/mol] | Chemical structures                                                                   |
|---------------------------|-------|--------------------------|---------------------------------------------------------------------------------------|
| Monochloroacetonitrile    | MCAN  | 75.50                    |    |
| Monobromoacetonitrile     | MBAN  | 119.95                   |    |
| Dichloroacetonitrile      | DCAN  | 109.94                   |    |
| Trichloroacetonitrile     | TCAN  | 144.38                   |    |
| Dibromoacetonitrile       | DBAN  | 198.85                   |   |
| Bromochloroacetonitrile   | BCAN  | 154.39                   |  |
| Dibromochloroacetonitrile | DBCAN | 233.29                   |  |

### 2.1.4 Haloacetamides (HAcAms)

Haloacetamides were initially identified as DBPs in drinking water in the US N-DBP survey in 2000-2002 (Weinberg et al. 2002; Krasner et al. 2006). Although they occur in low concentrations, usually ten times lower than HAAs (Krasner et al. 2006), HAcAms are currently the focus of research activity in the field, due to their reported risk of carcinogenicity and mutagenicity (Richardson et al. 2007; Plewa et al. 2008). According to Plewa et al. (2008) in a toxicology study reported that HAcAm were 142× and 12× more cytotoxic and genotoxic, respectively, than the five regulated HAAs, while in addition were 2 × more cytotoxic than the unregulated HANs. Regardless of the above findings, the nine chlorine- and bromine-containing haloacetonitriles presented in *Table 2.4* are not yet considered for future regulatory control. In

fact, limited information is available on HAcAms precursors and formation mechanisms, since it is a relatively new DBP group identified in drinking water.

Several studies postulate that HAcAms are ‘intermediate products’ of HANs hydrolysis, which can further degrade to the corresponding HAAs (Glezer et al. 1999; Reckhow et al. 2001; Bond et al. 2014), as illustrated below for the di-halogenated species (e.g. the di-HAN  $\rightarrow$  di-HAcAm  $\rightarrow$  di-HAA, with X representing a halogen):

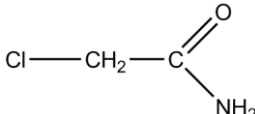
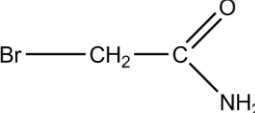
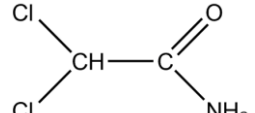
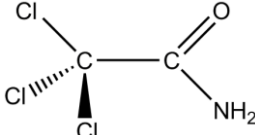
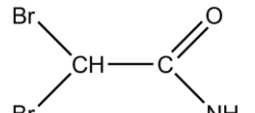
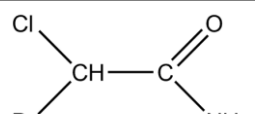
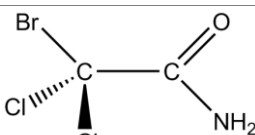
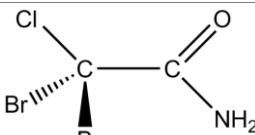
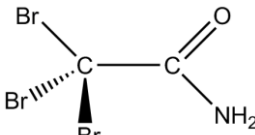


However, recently Huang et al. (2012) found that DCAcAm can be generated independently from DCAN during both chlorination and chloramination. The above study paved the way in investigating alternative pathways and potential nitrogenous and non-nitrogenous HAcAm precursors in drinking water during the application of chlorine and chloramines (Chu et al. 2010; Chu et al. 2010 (b); Kimura et al. 2013; Le Roux et al. 2016; Nihemaiti et al. 2016). Interestingly, the DCAcAm yields reported from model precursor studies, that include amino acids, are significantly lower than those of DCAN (Chu et al. 2010 (b)), whereas in studies that include real water matrices the levels of the two N-DBP groups are very similar (*median*: 1.4  $\mu\text{g/L}$  and 1  $\mu\text{g/L}$ , respectively)(Krasner et al. 2006). By assessing the two experimental approaches, it appears that still the majority of reported HAcAms occurrence is subjected to unknown precursors (Bond 2012). The highest formation potential for DCAcAm was identified in natural waters, represented by high yields of hydrophilic acid fraction (Chu et al. 2010), and further investigation by the same research group indicated that this fraction was characterised by protein-like structures, likely to be amino acids. In addition, Huang et al. (2012) and (2013) observed elevated HAcAms formation from algal (EPS) and wastewater impacted sources and bacterial cells during chloramination. Aromatic moieties of the natural organic fraction (i.e. resorcinol, phenol, various benzoic acids, tyrosine, phenylalanine) have also been investigated as potential N-DBP precursors, with the most reactive being resorcinol yielding a maximum of 0.83% in DCAcAm (Nihemaiti et al. 2016; Le Roux et al. 2016). Moreover, even though studies have discussed the potential of non-nitrogenous compounds; low molecular weight organic acids (Chu et al. 2016), aromatic compounds (Nihemaiti et al. 2016) and aldehydes (Kimura et al. 2013), to act as HAcAms precursors, knowledge gaps remain concerning the potential of inorganic nitrogen incorporation in these to form HAcAms.

To-date, in the UK and worldwide, there is very limited HAcAms occurrence data in actual finished water, which becomes even more finite in distribution systems. A 2011-2012 occurrence survey analysed multiple water samples from 20 water supply systems in the UK to identify HAcAms levels, among other N-DBPs (Templeton et al., 2012). The median reported concentration of total HAcAms (3 *species*) was 1.5 µg/L, with respective median levels of DCaAm and DBaAm at 0.6 µg/L and 0.7 µg/L (max: 4.5 µg/L and 5.1 µg/L). The results of this study indicated that total HAcAm concentrations (and those of the species individually) slightly increased between those identified in finished waters and the furthest downstream location of distribution (Bond et al. 2015). On the other hand, the US DBP survey monitored the occurrence of total HAcAms (5 *species*) in 12 water treatment works, and reported median and maximum levels of 2.8 µg/L and 7.4 µg/L, respectively (Krasner et al. 2006).

Nevertheless, the insufficiency in occurrence data of HANs and HAcAms in actual drinking water systems, is an important constraint in understanding whether HAcAms occur as HAN hydrolysis products, and to what extent, or they follow independent formation pathways.

**Table 2.4:** Characteristics of haloacetamides (HAcAms) monitored.

| HAcAms species         |        | Molecular weight [g/mol] | Chemical structures                                                                   |
|------------------------|--------|--------------------------|---------------------------------------------------------------------------------------|
| Monochloroacetamide    | MCaAm  | 93.51                    |    |
| Monobromoacetamide     | MBaAm  | 137.96                   |    |
| Dichloroacetamide      | DCaAm  | 127.96                   |    |
| Trichloroacetamide     | TCaAm  | 162.40                   |    |
| Dibromoacetamide       | DBaAm  | 216.86                   |   |
| Bromochloroacetamide   | BCaAm  | 172.40                   |  |
| Bromodichloroacetamide | BDCaAm | 206.85                   |  |
| Dibromochloroacetamide | DBCaAm | 251.30                   |  |
| Tribromoacetamide      | TBaAm  | 295.75                   |  |

Below, *Table 2.5* summarises the selected regulated and unregulated DBPs together with their typical occurrence levels, as these are reported in literature. This table highlights once more, the sparse knowledge on the occurrence of HANs and HAcAms and their species during water treatment but most importantly during water distribution.

**Table 2.5:** Total reported levels of selected regulated and unregulated DBPs during water treatment and distribution (Krasner et al. 1989; Weinberg et al. 2002; Krasner et al. 2006; Parsons and Goslan 2009; Mitch et al. 2009; Hrudey and Charrois 2012; Templeton et al. 2012; UKWIR 2014; Bond et al. 2015).

| DBPs Group               |        | Occurrence | Total Concentrations [µg/L] |                |
|--------------------------|--------|------------|-----------------------------|----------------|
|                          |        |            | Water Treatment             | Distribution   |
| <b>Trihalomethanes</b>   | THMs   | **         | 10-100                      | < 200          |
| <b>Haloacetic acids</b>  | HAAs   | **         | 10-80                       | < 100          |
| <b>Haloacetonitriles</b> | HANs   | *          | < 5                         | ~              |
| <b>Haloacetamides</b>    | HAcAms | *          | 2-3                         | ~              |
| *: low - mid µg/l levels |        | **:        | mid - high µg/l levels      | ~: sparse data |

## 2.2 Regulatory background of DBPs in drinking water

In November 1979, US Environmental Protection Agency set the first precautionary levels for the average annual concentration of the four THMs in drinking water at 100 µg/L. As research has provided more evidence regarding the possible health outcomes of DBPs exposure, US EPA reviewed these limits in two policy stages. According to 'Stage 1-disinfectants/disinfection by-products Rule', THM concentration limits were reduced to 80 µg/L and a limit of 60 µg/L for the average annual concentration of five HAAs (MCAA, DCAA, TCAA, MBAA and DBAA) was established (US EPA 1998). This stage was developed simultaneously with the 'Long Term 2-Surface Water Treatment Rule'(LT2) and attempted to elaborate a balance between pathogens control and health issues related to DBPs exposure by refining maximum contaminant levels (MCLs) for THMs, HAAs, bromate and chlorite. Stage 1 Rule was then updated by the Stage 2 Rule in 2006 (US EPA 2006) when limits for bromate and chlorite were also set at 10 µg/L and 10 mg/L, respectively.

At the same time the World Health Organization (WHO) has also established guidelines for DBPs concentrations in drinking water that incorporated NDMA and haloacetonitriles levels. The recommended guideline values for two HAN species, DBAN and DCAN are at 70 µg/L and 20 µg/L, respectively, whereas for NDMA is 0.1 µg/L (WHO 2011b).

The European Union has published Directive 98/83/EC concerning water quality for human consumption which aims to protect human health by setting some quality standards. Among other water quality parameters, the Directive has only determined total THMs and bromate levels, for the case of DBPs at 100 µg/L and 10 µg/L, respectively (EU 1998). Therefore, the UK regulatory framework for drinking water has integrated these levels, according to which water utilities are being regulated and monitored. In 2012, the Drinking Water Inspectorate (DWI 2012) stated that for PR14 water companies must show that they; 'design, operate and maintain the disinfection process so as to keep disinfection by-products as low as possible without compromising the effectiveness of the disinfection'. In addition, currently the European Union is considering regulating the nine major HAAs (chlorine/bromine types) at 80 µg/L (Jørgensen et al. 2008) which if applied may pose substantial alterations and challenges for UK water utilities. A published DWI/ DEFRA report postulated that water utilities in England and Wales should expect a high number of exceedances if HAAs regulation levels are set at even lower levels than the proposed (Jackson et al. 2008).

Furthermore, various other countries have introduced DBPs regulations, such as Australia, Japan and Canada which have moved one step forward and have even regulated some types for the first time (NDMA, cyanogen chloride, formaldehyde) (Health Canada 2009; Japanese Ministry of Health 2010; NHMRC and NRMMC 2011). The maximum permissible concentrations of the regulated DBPs in various countries and the recommended guidelines are given in **Table 2.6**, below.

An interesting point is that even though literature has identified hundreds of by-products and their possible health outcomes, some DBP groups considered to be more genotoxic and cytotoxic have not been yet formally regulated by large governmental bodies. Indeed, there are nearly 70 additional DBPs that occur at concentrations similar to those at which the main 11 regulated DBPs (THMs and HAAs) occur (DeMarini 2011).

**Table 2.6:** Regulatory and guideline limits for DBPs in drinking water worldwide (EU 1998; Health Canada 2009; Japanese Ministry of Health 2010; NHMRC and NRMMC 2011; WHO 2011b).

| Country/Agency                                                                                                                | DBPs                           | Limit value [µg/L] |
|-------------------------------------------------------------------------------------------------------------------------------|--------------------------------|--------------------|
| <b>World Health Organisation</b>                                                                                              | Chloroform                     | 300                |
|                                                                                                                               | Bromodichloromethane           | 60                 |
|                                                                                                                               | Chlorodibromomethane           | 100                |
|                                                                                                                               | Bromoform                      | 100                |
|                                                                                                                               | Monochloroacetic acid          | 20                 |
|                                                                                                                               | Dichloroacetic acid            | 50                 |
|                                                                                                                               | Trichloroacetic acid           | 200                |
|                                                                                                                               | Bromate                        | 10                 |
|                                                                                                                               | Chlorate                       | 700                |
|                                                                                                                               | Chlorite                       | 700                |
|                                                                                                                               | Dichloroacetonitrile           | 20                 |
|                                                                                                                               | Dibromoacetonitrile            | 70                 |
|                                                                                                                               | <i>N</i> -Nitrosodimethylamine | 0.1                |
| <b>US Environmental Protection Agency</b>                                                                                     | Total THMs                     | 80                 |
|                                                                                                                               | HAA5                           | 60                 |
|                                                                                                                               | Bromate                        | 10                 |
|                                                                                                                               | Chlorite                       | 1000               |
| <b>European Union</b>                                                                                                         | Total THMs                     | 100                |
|                                                                                                                               | Bromate                        | 10                 |
| <b>Australia</b><br><i>(National Health and Medical Research Council and Natural Resource Management Ministerial Council)</i> | Total THMs                     | 250                |
|                                                                                                                               | Monochloroacetic acid          | 150                |
|                                                                                                                               | Dichloroacetic acid            | 100                |
|                                                                                                                               | Trichloroacetic acid           | 100                |
|                                                                                                                               | Trichloroacetaldehyde          | 20                 |
|                                                                                                                               | Cyanogen chloride              | 80                 |
|                                                                                                                               | Bromate                        | 20                 |
|                                                                                                                               | Chlorite                       | 800                |
|                                                                                                                               | <i>N</i> -Nitrosodimethylamine | 0.1                |
| <b>Japan</b><br><i>(Ministry of Health, Labour and Welfare)</i>                                                               | Total THMs                     | 100                |
|                                                                                                                               | Chloroform                     | 60                 |
|                                                                                                                               | Bromodichloromethane           | 30                 |
|                                                                                                                               | Chlorodibromomethane           | 100                |
|                                                                                                                               | Bromoform                      | 90                 |
|                                                                                                                               | Bromate                        | 10                 |
|                                                                                                                               | Monochloroacetic acid          | 20                 |
|                                                                                                                               | Dichloroacetic acid            | 40                 |
|                                                                                                                               | Trichloroacetic acid           | 200                |
|                                                                                                                               | Formaldehyde                   | 80                 |
| <b>Canada</b><br><i>(Health Canada)</i>                                                                                       | Total THMs                     | 100                |
|                                                                                                                               | HAA5                           | 80                 |
|                                                                                                                               | Bromate                        | 10                 |
|                                                                                                                               | Chlorate                       | 1000               |
|                                                                                                                               | Chlorite                       | 1000               |
|                                                                                                                               | <i>N</i> -Nitrosodimethylamine | 0.04               |

## 2.3 Factors affecting the concentrations of regulated and unregulated DBPs in distribution

Numerous water quality and disinfection factors are responsible for enhancing or limiting DBPs occurrence in drinking water networks, and influence their speciation. These include the amount and nature of precursors, the disinfectant practice, water temperature and age, pH, and bromide levels. The combining effect and the extent to which these affect DBPs formation varies among the classes and is still an ongoing research field, with the main findings summarized in **Table 2.7**.

### 2.3.1 Impact of organic precursors

DBP precursors may be present either as natural organic matter from aquatic biota and/or terrestrial watershed (non-humic and humic substances), organic materials in water mains, or chemical additives during water treatment processes (Bond 2012; Bond et al. 2014; Krasner et al. 2015). The varying degree of their concentration, hydrophilicity, chemical structure, and molecular weight determines the DBPs levels and speciation in drinking water, and depend on seasonality, topography and water treatment efficiency (Mitch et al. 2009; Bond et al. 2012). THMs and HAAs precursors typically stem from humic and non-humic substances, characterised of polar and hydrophobic character, whereas the primary source of HANs and HAcAms precursors is nitrogenous-rich structures (Croue et al. 2000; Bond et al. 2012 (a-b); Nihemaiti et al. 2016). The concentration of the organic material present in water matrices is usually measured as total organic carbon (TOC), dissolved organic carbon (DOC), while the nature is monitored by calculating SUVA values. Generally, high TOC levels, or DOC levels are associated with increased THMs and HAAs formation (US Environmental Protection Agency 2006). Singer and Chang (1989) obtained data from 12 full-scale plants and reported good correlations between TOC values and THMs formation ( $r=0.83$ ) in finished waters, however this correlation was significantly lower in distribution systems. Obolensky and Frey (2002) postulated that surface water plants characterized by inadequate coagulation or filtration practices, thus poor precursor removal and high TOC, reported 90<sup>th</sup> percentile HAAs level of 60 µg/L, whereas groundwater plants reported median level of 13 µg/L. Nevertheless, the quantity and quantity of organic precursors is seasonally dependent (Singer 1999), due to soil decomposition, rainfalls or other aquatic discharges. In any case, water utilities do not have any action tools to correct fluctuations of the organic matter content in raw water, and therefore face significant seasonal variances in DBP levels in distribution systems (Meyer 1992; Baribeau et al. 2006). In fact, Meyer (1992) measured that in the same

water treatment plant a 10% precursor removal was reported during winter whereas this was 65% during summer, which indicated the different seasonal precursor loading in water reservoirs. According to Nguyen et al. (2002) the content of the dissolved organic matter was reported to be elevated during the late summer run-offs and spring snowmelts, with DOC values ranging from 3 to 7 mg/L, which was linked with an increase of HAAs precursors by approx. 90% in water reservoirs. Also, the significant increase of organic content leads to increased disinfectant demand in water treatment plants, and thus higher disinfectant doses to achieve regulatory compliance, already reported to encourage THMs, HAAs and HANs formation (Obolensky and Frey 2002; UK WIR 2014). Moreover, the formation of nitrogenous DBPs, including HANs and HAcAms, is reported to be elevated in wastewater impacted or algal-rich water matrices that contain nitrogen organic fractions (Dotson et al. 2009). Several researchers have investigated the potential of these nitrogen-rich species, such as amino acids (both aliphatic and aromatic), proteins, pyrroles, pyrimidines, lignin phenols to act as N-DBPs precursors by chlorinating and chloraminating model precursor compounds (Chu et al. 2010; Bond et al. 2014; Chuang et al. 2015; Le Roux et al. 2016; Nihemaiti et al. 2016). A recent publication highlighted that the presence of aromatic moieties in the precursor pool, expressed with high SUVA value, encouraged the formation of N-DBPs in comparison with the samples of high aliphatic content during chloramination (Le Roux et al. 2016), even without nitrogenous precursors via inorganic nitrogen incorporation. In fact, the most reactive precursors were the non-nitrogenous compounds, resorcinol and phenol, that yielded respectively, 1.14 %M/M and 4.4 %M/M of DCAN, while 0.83 %M/M and 0.22 %M/M of DCACAm were formed. However, according to Thurman (1985) and Świetlik et al. (2004), the nitrogenous amine and amide substances are abundant in natural surface water and sediments, consist with a substantial ratio of dissolved organic matter, and represent around 3% of NOM. Bond et al. (2014), assessed the effect of both chlorination and chloramination of seven model amine compounds in three pH values (6, 7 and 8), and identified concentrations of DCAN, TCAN, chloroform and TCNM. Chu et al. 2010 investigated the formation of DCACAm from 20 amino acids during chlorination and chloramination, of which the most reactive being aspartic acid, followed by histidine with corresponding yields of 0.23 and 0.19 % M/M. However, the least reactive amides have never been directly oxidized to investigate their potential to function as HAcAms, HANs or other DBPs precursors and consists of a knowledge gap.

**Table 2.7:** Main formation factors of DBPs of water utilities interest and their expected corresponding occurrence trends (adapted from Chen and Weisel 1998b; Krasner et al. 2006; Yang et al. 2007; Sadiq and Rodriguez 2004; Hrudey and Charrois 2012; Templeton et al. 2012; UK WIR 2014).

| DBPs Formation Factors                                                  | THMs | HAAs            | N-DBPs         | HANs            | HAcAms          | NDMA | Bromate         |
|-------------------------------------------------------------------------|------|-----------------|----------------|-----------------|-----------------|------|-----------------|
| Concentration of disinfectant                                           | ↑    | ↑               | ~              | ❖               | ~               | ~    | ↑               |
| Disinfectant contact time                                               | ↑    | ↑↓ <sup>a</sup> | ~              | ~               | ~               | ↑    | ↑               |
| Concentration of organic/ inorganic matter                              | ↑    | ↑               | ↑ <sup>b</sup> | ↑               | ↑               | ↑    | ↑↓ <sup>b</sup> |
| Bromide ions (Br <sup>-</sup> )                                         | ↑    | ↑               | ~              | ↑               | ↑               | ↑    | ↑               |
| Water temperature                                                       | ↑    | ↑               | ~              | ~               | ~               | ↑    | ↑               |
| pH                                                                      | ↑    | ↓               | ↑↓             | ↑↓ <sup>c</sup> | ↑↓ <sup>d</sup> | ↑↓   | ↑               |
| Water age (Distribution size)                                           | ↑    | ↑↓ <sup>a</sup> | ~              | ~               | ~               | ↑    | ~               |
| ↑ : Increase      ↓ Decrease      ❖ : No effect      ~: Sparse evidence |      |                 |                |                 |                 |      |                 |

a. Biodegradation (Zhang et al., 2009; Bayless et al., 2008).

b. Depends on the NOM content (algae, blended with treated wastewater effluent) (Bond et al., 2012).

c. Decreases at higher pH (>7) / Less stable at lower pH (Templeton et al., 2012; UWIR, 2013).

d. Decreases at lower pH (<5)/ Less stable at higher pH (Templeton et al., 2012; UWIR, 2013).

### **2.3.2 Impact of disinfection practice**

All the reactions between water constituents and the selected disinfectant are considerably affected by several water quality (pH, temperature) and operational parameters (doses, residence time, water flow). While the most common practice of chemical disinfectants in drinking water is chlorination, alternative practices are increasingly being implemented by water utilities (US Environmental Protection Agency 2010), such as chloramination, chlorine dioxide, ozonation and UV disinfection, to control the formation of DBPs. Indeed, several studies have investigated the potential of chloramines to limit the formation of regulated THMs and HAAs (Karanfil et al. 2007; Bougeard et al. 2010). Literature suggests that the levels of THMs formed during chloramination are usually 20% less than those formed during chlorination (Cowman and Singer 1996; Diehl et al. 2000). A study that included 7 water treatment plants from Scotland concluded that generally HAA were significantly higher in treatment works applying chlorine in comparison with those applying chloramines (Goslan et al. 2009). Nevertheless, the implementation of chloramines has been associated with increased levels of N-DBPs (Mitch et al. 2003; Bond et al. 2011; Krasner et al. 2012; Huang et al. 2017). Concerning the target N-DBPs, HANs and HAcAms, literature findings are conflicting. The UK N-DBPs survey reported that both HANs and HAcAms concentrations in chloramination were lower than chlorination (Templeton et al. 2012). On the other hand, Huang et al. (2017) argued that chloramines (pre-formed) generated higher levels of HAcAms and lower levels of HANs, while in-line chloramines generated the highest levels in both N-DBPs classes. However, Mitch et al. (2009) reported that the differences between HANs concentrations upon chlorination and chloramination were not significant.

It has to be noted, though, that according to Xie et al. (2004), all current disinfection practice have been reported to generate DBP formation in varying degrees and therefore water utilities have no option to opt for a DBP-free disinfection.

### **2.3.3 Impact of water temperature**

As mentioned above, the amount and nature of organic precursors, and disinfectant dose may vary seasonally, as water temperature fluctuates, which in turn influences DBP occurrence and behavior in distribution. Several researchers have reported strong correlations between the increased occurrence of THMs, HAAs, and HANs in waters of high temperatures, namely during summer, and the opposite during water of low temperatures (Krasner et al. 1989; Singer 1999; Baribeau et al. 2006; Graham et al. 2009;

Bond et al. 2012). However, more recent studies argued that the formation of N-DBPs, such as HANs and HAcAms, is not seasonally dependent, and similar concentrations were reported during all seasonal samplings (Templeton et al. 2012; Bond et al. 2015). Apart from those, increasing water temperatures are reported to accelerate the rate of chemical reactions within distribution systems, and thus form or decompose DBPs more rapidly (Baribeau et al. 2006). Indeed, the biodegradation of HAAs and HANs hydrolysis was more pronounced when water temperature was high and the free chlorine was low ( $<0.5$  mg/LCl<sub>2</sub>), as previously discussed by many researchers (Koch et al. 1991; Rossman et al. 2001; Symanskiet al. 2004; Baribeau et al. 2006; Shi et al. 2017).

### **2.3.4 Impact of pH**

In full-scale distribution systems, elevated pH values have been observed to increase THM concentrations and decrease tri-HAAs levels, while di-HAAs are reported to be relatively unaffected from pH alterations (Bond et al. 2012). Reckhow et al (1990) suggests that higher pH levels favor base catalyzed hydrolysis of the halogenated leaving group and thus encourage the formation of the above classes. Nevertheless, the impact of pH on the formation of N-DBPs is not conclusive with the existing literature, but a general pattern is that; HANs are more stable at acidic pH and more prone to hydrolysis at alkaline pH (Oliver 1983; Glezer et al. 1999), whereas HAcAms present the same pattern as HANs but are characterised by lower occurrence in acidic pH (Reckhow et al. 2001; Krasner et al. 2006; Chu et al. 2010). Among the HANs species, even though hydrolysis rates increase with increasing pH values, tri-HANs are more susceptible to degradation than di-HANs (Glezer et al. 1999; Reckhow et al. 2001). On the other hand, upon chloramination THMs formation has been reported to be decreased at alkaline pH, both in natural waters and model compound experiments (Diehl et al. 2000; Bond et al. 2014), whereas information on pH-mediated effect on N-DBPs during chloramination is limited. More specifically, the formation of DCAN upon chloramination has been reported to be less affected by pH-mediated effect between pH values of 7.5-9 (Joo and Mitch 2007), while DCAcAm and TCAcAm stability was similar to that during chlorination (Chu et al. 2010).

### **2.3.5 Impact of bromide**

Generally, the presence of bromide ions in water has been widely associated with elevated halogenated DBPs in both chlorinated and chloraminated systems (Cowman and Singer 1996; Baribeau et al. 2006; Krasner et al. 2008; Chu et al. 2013). In addition, increasing bromide levels result in changes in chlorine to bromine ratios and thus shift speciation towards more brominated DBP species (Symons et al. 1993;

Krasner et al. 2008). Brominated DBPs are suspected of being more toxic than their chlorinated counterparts (Plewa et al. 2008), and therefore is crucial to comprehend the role of bromine incorporation in regulated and regulated DBPs. Besides, HOBr is considered as more efficient halogen substitution agent than chlorine and bromine has higher reactivity than chlorine (Symons et al. 1993; Cowman and Singer 1996). Amy et al. (1991) in a study that included natural water samples, observed that 5-10% of HOCl was incorporated in THMs, while bromine was incorporated by approx. 50% in DBPs. Hua and Reckhow (2012) calculated the BIFs for four DBP classes (THMs, di-HAAs, tri-HAAs and di-HANs) and postulated that these decreased with increasing retention time and temperature during both chlorination and chloramination. Even though pH had no effect in the bromine incorporation the order of BIFs were DHAN > THM & di-HAA > tri-HAA upon chlorination, whereas upon chloramination HAAs exhibited higher BIF values. There is little information on the role of bromide ions in the formation of N-DBPs, since the majority of model compound surveys do not include bromide spiking even though natural waters are characterised by varying levels of bromide of 20-400 µg/L (Krasner et al. 2006). Exception to the above are the separate N-DBP studies by Bond et al. (2009) and (2015) that calculated BIF values and concluded that during chlorination di-HAcAms present higher BIF than di-HANs, whereas during chloramination even though BIFs for di-HAcAms were lower than di-HANs BIF, both were significantly higher than in chlorination. The methodology by which BIF values are usually calculated, both in the above and the current study, can be found in Chapter 4.6.

### **2.3.6 Impact of water age**

Water age is an indication of the residence time in distribution between the treatment plant and the consumer, which encompasses water flow rate, demand, network length, and configuration of downstream locations (Tinker et al. 2009; Shu et al. 2010) and is usually estimated by hydraulic models. Increased water ages in water distribution systems means increased reaction time between the disinfectant and the bulk of water in pipes; since the formation of most DBPs continues as long as disinfectant residual is present in distribution networks, the levels of DBPs in customer taps are affected by water age (US Environmental Protection Agency 2010). Koch et al. (1991), performed SDS tests and reported that THMs, HAAs and HANs increased with increasing water age, between 2 and 100 hours, with the two-latter presenting intermediate decreases. In line with the above study, Chen and Weisel (1998) found that the formation of THMs was increasing with water age, whereas HAAs formation was decreasing between 24-72 hours. A nationwide US survey that included sampling from both full scale systems and SDS tests concluded that

the sum of THMs significantly increased by median 70% in chlorinated systems between 0-323 hours, while HAAs increased or remain stable with water age and presented decreases at >120 hours (Baribeau et al. 2006). One of the main caveats to understand the behavior of DBPs in distribution is the fact that studies use limited and different water ages, or even include distance instead, and therefore the conclusions concerning the overall impact of water age in DBP levels is usually conflicting. Information about the fate of N-DBPs as a function of water age, and especially for HAcAms is very limited; although, it suggests that HAcAms (DCAcAm, DBAcAm, TCACAm) levels may slightly increase in distribution (Bond et al. 2015).

### **2.3.7 Impact of other distribution network characteristics**

It is possible for the disinfectant residual to be consumed by water pipe materials or other corrosion materials, with iron pipes reported to be highly reactive with chlorine resulting in increased chlorine demand in distribution and subsequently increased DBP formation (Vasconcelos et al. 1997; Kiéné, Lu, and Lévi 1998). Also, reducing agents present in pipe materials, such as iron and/or sulphite, are reported to result in HAAs degradation (Hozalski et al. 2008). There is limited information on the effect of water pipe diameter in the formation of DBPs, although, Vasconcelos et al. (1997) stated that the rate of chlorine reactions were inversely associated to the diameter of the pipes, which suggests potential deviations in DBP occurrence between narrow and wide water pipes. However, Baribeau et al. (2006) investigated the effect of pipe diameters in two full scale distribution networks and reported poor correlation between the concentrations of dissolved organic matter and pipe dimensions. As far as the distribution system hydraulics are concerned, it is known that water flow, pressure and residence time influence water quality and possibly DBP behavior, yet literature contains sparse information. It is known, though, that low water flows, and even worse stagnation, increases biofilm growth, nitrification and disinfectant consumption, whereas high water flows accelerate disinfectant transportation and reactions, and biomass disintegration (LeChevallier et al. 1990; Baribeau et al. 2006; Idornigie et al. 2010).

## 2.4 Strategies for minimising DBPs

To-date, several studies have been published concerning the mitigation strategies of disinfection by-products. Among them, enhanced precursor removal, modification and optimisation of treatment and disinfection practices and DBP removal after formation have been the most widely applied operational strategies.

These strategies that can be implemented can be classified into two main categories; the ‘*prevention*’ strategies, which may proactively be applied to limit DBPs formation and the ‘*treatment*’ strategies, which may remove DBPs after their formation. The main ‘*prevention*’ strategies, as found in literature, can be organised as follows:

- ◆ Control and protection of the water source – catchment management for algal control (Singer 1999; WHO 2009; UK WIR 2014).
- ◆ Precursor removal (US EPA 2010; Bond et al. 2012 a and b; UKWIR 2014) using the following methods individually or in combination:
  - *Enhanced Coagulation* (Krasner and Amy 1995; Crozes et al. 1995; Uyak and Toroz 2005; Chowdhury et al. 2009; Krasner et al. 2013).
  - *Adsorption on Granular Activated Carbon (GAC)* (Mcguire et al. 1991; Chowdhury et al. 2009; Hrudey and Charrois 2012; Krasner et al. 2013).
  - *Addition of Powdered Activated Carbon (PAC)* (Uyak et al. 2007; Dunn and Knappe 2013).
  - *Membrane filtration* (LeChevallier et al. 1992; Laine et al. 1993; Lin et al. 1999; Krasner 2009).
  - *Reverse Osmosis* (Mitch et al. 2003; Gyparakis and Diamadopoulos 2007; Lugg et al. 2009; Farré et al. 2010).
  - *Magnetic Ion Exchange (MIEX®)* (Singer and Bilyk 2002; Mergen et al. 2008; Cousins 2013; Boyer 2015).
  - *Advanced oxidation processes (AOPs)* (Chin and Bérubé 2005; Lamsal, Walsh, and Gagnon 2011).
  - Other methods - *Lime softening* (Thompson et al. 1997; Krasner 2009), *Slow sand filters* (Collins et al. 1992; Moncayo-Lasso et al. 2008), *Adsorption by cyclodextrin nanoporous polymers* (Mhlongo et al. 2009), *Riverbank filtration* (Weiss et al. 2003; Jaramillo 2012).

- ◆ Use of alternatives disinfectants, e.g. chloramines, chlorine dioxide, UV, ozone (Jacangelo et al. 1989; Singer 1994; Krasner et al. 2006; USEPA 2010).
- ◆ Effective management of the distribution system (US EPA 2010; UKWIR, 2013; Wang et al., 2013; USEPA 2012; UK WIR 2014).

On the other hand, ***‘DBP removal’*** strategies can be implemented by water utilities after the initial DBP formation to eliminate those generated in drinking water (EU 1997):

- ◆ Deflation in towers with filler.
- ◆ Air stripping (for volatile DBPs).
- ◆ Activated carbon adsorption.
- ◆ Biodegradation.
- ◆ High-energy electron-beam irradiation (Cooper et al. 1993).
- ◆ Removal at entry point or point of use (e.g. by household carbon filters or leaving water to sit in a jug in the fridge to volatilise THMs).

According to the USEPA Drinking Water Guidance on Disinfection By-Products (USEPA 2010), activated carbon adsorption and alternative disinfection have been proved to be effective for the minimisation of some DBPs during water treatment (Hrudey et al., 2012). However, the type of mitigation strategy and the performance level varies according to the target DBP. Currently, GAC adsorption is being extensively tested by water utilities to inform updated formation potential and subsequent current efficacy of organic and inorganic DBP precursor removal through the process, as until now it is used predominately for the removal of pesticides, taste and odour compounds (WHO 2011b). However, recent research concluded that GAC can be optimised for future DBP removal by improved adsorption capacity of current GAC absorbers, thus increased regeneration frequency (Spellman 2015).

## 2.5 Simulated distribution system (SDS) tests

After the adoption of regulations for THMs in the US (1978) and in Europe (1980) there was a need for water utilities and engineers to create an evaluating tool to understand further the occurrence of these compounds in their water matrices. For this reason, trihalomethane formation potential tests (FP), which is a standardised method (5710B) (APHA 1999), were initially implemented to estimate the formation of THMs, and later of HAAs. However, FP tests albeit being rapid and accurate were mainly evaluating the impact of precursors and treatment processes in the formation of DBPs, rather than predict formation in distribution systems and tap waters (Xie and Xie 2004). Its main characteristics - long incubation time (7 days), high incubation temperature ( $25 \pm 2^\circ\text{C}$ ) and excess of chlorine residual (3-5 mg/L), indicate the FP test tendency to overestimate operational DBP concentrations and do not replicate DBP formation during actual treatment conditions (Reckhow and Edzwald 1991; Brereton and Mavinic 2002). Indeed, several papers have reported elevated DBPs concentrations from FP tests when compared against actual field samples (Krasner et al 2007; Bougeard et al. 2010). On the other hand, the relative brominated species have been reported to be lower, due to the lower Br/Cl ratio in excess chlorine (Chen and Westerhoff 2010). Therefore, in the early 1990s, Simulated Distribution System tests (SDS) were developed and validated as the most appropriate method to realistically predict the formation of trihalomethanes (THMs) in real distribution systems (Koch et al. 1991). In this study, filtered effluent water samples from two different plants were collected, which were then dosed in the lab with chlorine (representative of plant dosage) and incubated in typical distribution temperatures for up to 5 days (6 intermediates), see Chapter 4.2. The results of this study showed that these tests are a promising tool for researchers and water utilities, if the setup parameters are adjusted, to predict the amount of DBPs in various locations in their supply zones. Since then, these tests are recommended by the US EPA to American water utilities and have been implemented in many US studies, and in a lesser extent in Europe, to collect abundant DBP information in downstream locations. Krasner et al. (2011) refers to SDS tests as a method that ‘mimics’ operations and water quality conditions in distribution systems, with reported correlations against real water samples of 0.91, 0.81, 0.98 ( $R^2$  value) for THMs, DXAAs and TXAAs, respectively. Previous studies have shown that SDS estimated well the levels of THMs, HAAs, HKs and NDMA, both in chlorinated and chloraminated systems (Koch et al. 1991; Krasner et al. 1994; Rossman et al. 2001; Baribeau et al. 2006; Graham et al. 2009; Zhang et al. 2011; Krasner et al. 2011). Apart from this, SDS test is also useful as a means of considering the impact of potential changes to distribution practices, such as switching from chlorination to chloramination, on the

expected DBP formation. Andrews et al. (2005) performed SDS tests by using real water matrices to investigate the changes in THMs and HAAs concentrations when replacing chlorine with chlorine dioxide in the selected water works.

To the author's knowledge the present study is the first time SDS tests are being implemented to predict the formation of HAcAms and HANs in chlorinated and chloraminated systems, and simultaneously evaluate the impact of future operational alterations.

The SDS tests are performed using a simple and inexpensive lab-based technique (batch incubation in bottles), simulating *four* major parameters; effluent water constituents, water conditions (pH, temperature), disinfectant residuals and water ages of a distribution system, allowing sampling at prescribed time intervals for analysis of DBP formation. Moreover, these tests provide a few key **advantages** over sampling programmes from real distribution systems, namely (US EPA 1997):

- It allows realistic assessment of DBP levels in site specific location, even before commissioning, so that necessary operational adjustments could be done proactively.
- It allows you to predict DBP levels that would result from proposed operational changes in distribution practices, which might be impossible to test in the real distribution system.
- It allows you to quantify a range of different DBPs and other relevant water quality parameters (e.g. pH, temperature, bromide, chlorine residual) in the same sample taken at the same time, which is not common when assessing historical data from various field sampling programmes.
- It gives an accurate knowledge of and control over water age when determining the DBPs, i.e. samples could be quenched in specific time intervals, which is beneficial since determination of residence time in real systems is often complex, uncertain or even unknown.
- It allows you to easily look at the effect of booster chlorination on DBPs, i.e. by dosing chlorine into the sample after a prescribed amount of time to simulate where/when this would occur in the real system.
- The tests are more cost-effective, less time intensive, and involve less manpower than sampling from the real distribution system and modelling water age computationally.

However, the nature of this laboratory batch incubation may not always represent the behaviour of DBPs in actual large-scale systems because of several limitations. Indeed, information to date argues that SDS tests do not account for all the in-situ conditions of a distribution network, which may be relevant for some DBPs; effect of pipe walls, biofilm built up and dynamic nature of pipes (Rossman et al. 2001; Reckhow

et al. 2016), and subsequently assess their potential impact on DBP formation. Reducing agents present in pipe materials, such as iron and/or sulphite, result in HAAs degradation (Hozalski et al. 2008). In addition, degradation of halogenated compounds may also be triggered by biotic reactions, typically increased with the presence of bacteria found in biofilms (McRae et al. 2004; Zhang et al. 2009; Wang et al. 2013). Metallic pipe corrosion products and biofilm growth may also exert significant chlorine demand and thus leave less residual disinfectant to react with NOM to form DBPs (Vasconcelos et al. 1997; Ki  n   et al. 1998; Frateur et al. 1999). Finally, bottle incubation may not fully represent mixing and hydraulic conditions of a distribution and thus simulate the reaction rates (Rossman et al. 2001). Nevertheless, each experimenter may modify the experimental setup (eg. apply continuous mixing) and as such minimise the above limitations.

## 2.6 Empirical models for DBPs

During the past three decades, research on the field has also attempted to develop empirical models to predict the formation of DBPs in drinking waters. The numerous models reported include the correlation of the impact of operational and water quality parameters in generating DBPs under numerous environmental conditions and/or formation kinetics, either from databases of actual water samples (raw, pre-treated) or artificial water matrices (Golfinopoulos et al. 1998; Amy et al. 1998; Villanueva et al. 2003; Rodriguez et al. 2003; Nikolaou et al. 2004; Uyak et al. 2007; Ghebremichael et al. 2008). The implementation of these predictive models by water utilities and researchers could be a useful mathematical tool to assess the impact of operational treatment strategies or water quality management in drinking water works, and/or assess the health risk due to DBP exposure of their customers.

Since 1983, more than 55 scientific studies have reported approximately 150 models that have been suggested to primarily predict the formation of THMs and HAAs, and to a lesser extent that of HANs, bromate and chlorite. A comprehensive summary of the statistical models to predict DBPs formation, organised by chronological order, can be found in **Table 2.8**. The majority of the proposed models have been derived using empirical relationships among the various parameters and DBP levels, and linear regression analysis, even though formation models have been developed based on kinetic relationships (Engerholm and Amy 1983; Adin et al. 1991; Clark and Sivaganesan 1998; Golfinopoulos and Arhonditsis 2002; Gang et al. 2002). However, the diversity of water sources selected in combination with the variability of experimental conditions in each study results significant differences between the proposed

statistical models. In addition, some modellers have not considered several DBP formation factors, possibly determinative, due to data scarcity.

**Table 2.8:** Summary of studies including empirical models for the prediction of DBPs (and other) in drinking water in chronological order (adapted from (Chowdhury et al. 2009)).

| DBPs investigated                        | R <sup>2</sup>        | References                           |
|------------------------------------------|-----------------------|--------------------------------------|
| THMs                                     | >0.90                 | (Minear and Morrow 1983)             |
| THMs                                     | n/a                   | (Urano et al. 1983)                  |
| CHCl <sub>3</sub>                        | n/a                   | (Engerholm and Amy 1983)             |
| THMs                                     | n/a                   | (Morrow and Minear 1987)             |
| THMs                                     | 0.90                  | (Amy et al. 1987)                    |
| THMs                                     | 0.90                  | (Adin et al. 1991)                   |
| Brominated THMs                          | 0.97                  | (Chowdhury et al. 1992)              |
| THMs                                     | n/a                   | (Harrington et al. 1992)             |
| CHCl <sub>3</sub> , BDCM, DBCM           | n/a                   | (Malcolm Pirnie Inc. 1992)           |
| THMs                                     | n/a                   | (Malcolm Pirnie Inc. 1993)           |
| THMs, HAA5                               | 0.80-0.92, 0.80-0.98  | (Montgomery 1993)                    |
| THMs                                     | n/a                   | (Lou and Chiang 1994)                |
| CHCl <sub>3</sub>                        | 0.82                  | (Ibarluzea et al. 1994)              |
| Bromate (BrO <sub>3</sub> <sup>-</sup> ) | n/a                   | (Ozekin 1994)                        |
| Bromate, CHBr <sub>3</sub> , TOBr        | 0.64-0.93, 0.78, 0.95 | (Siddiqui et al. 1994)               |
| Bromate (BrO <sub>3</sub> <sup>-</sup> ) | 0.93                  | (Song et al. 1996)                   |
| THMs, NPOX                               | 0.98                  | (Rathbun 1996)                       |
| THMs                                     | 0.94-0.97             | (Chang et al. 1996)                  |
| CHCl <sub>3</sub>                        | 0.65-0.86             | (Garcia-Villanova et al. 1997)       |
| POX, NPOX                                | 0.92-0.94             | (Huixian et al. 1997)                |
| THMs                                     | 0.71                  | (Clark and Sivaganesan 1998)         |
| THMs                                     | 0.98                  | (Golfinopoulos et al. 1998)          |
| THMs, HAA6                               | n/a                   | (Amy et al. 1998)                    |
| THMs                                     | n/a                   | (Nokes et al. 1999)                  |
| THMs                                     | 0.34-0.90             | (Rodriguez et al. 2000)              |
| THMs                                     | n/a                   | (Milot et al. 2000)                  |
| THMs, HAA5                               | 0.93, 0.74            | (Sung et al. 2000)                   |
| THMs                                     | n/a                   | (Westerhoff et al. 2000)             |
| THMs                                     | n/a                   | (Elshorbagy et al. 2000)             |
| THMs, HAA                                | 0.95                  | (Clark et al. 2001)                  |
| THMs                                     | 0.51-0.62             | (Golfinopoulos and Arhonditsis 2002) |
| Chlorite, Chlorate                       | 0.95                  | (Korn et al. 2002)                   |
| THMs, HAAs                               | n/a                   | (Gang et al. 2002)                   |
| THMs, HAAs                               | 0.78, 0.92            | (Sérodes et al. 2003)                |
| HAA9                                     | 0.57-0.97             | (Villanueva et al. 2003)             |
| THMs, HAAs                               | 0.38-0.58, 0.28       | (Nikolaou et al. 2004)               |
| THMs                                     | n/a                   | (Al-Omari et al. 2004)               |

|                                                                                     |                                 |                                   |
|-------------------------------------------------------------------------------------|---------------------------------|-----------------------------------|
| THMs, HAA6, TOBr                                                                    | 0.70-0.92, 0.80-0.94, 0.95-0.98 | (Sohn et al. 2004)                |
| THMs, DCAN, TCP                                                                     | 0.77, 0.69, 0.68                | (Boyalla 2004)                    |
| THMs, HAAs                                                                          | 0.87, 0.51                      | (Lekkas and Nikolaou 2004)        |
| THMs                                                                                | 0.98                            | (Uyak and Toroz 2005)             |
| Bromate                                                                             | 0.80                            | (Tyrovola and Diamadopoulos 2005) |
| CHCl <sub>3</sub> , CAA                                                             | n/a                             | (Chang et al. 2006)               |
| THMs                                                                                | 0.99                            | (Chaib and Moschandreas 2006)     |
| DCAA                                                                                | 0.81-0.96                       | (Duirk and Valentine 2006)        |
| THMs                                                                                | n/a                             | (Rodrigues et al. 2007)           |
| THMs                                                                                | 0.87                            | (Hong et al. 2007)                |
| THMs, HAAs                                                                          | 0.61                            | (Uyak et al. 2007)                |
| Bromate                                                                             | 0.77-0.84                       | (Civelekoglu et al. 2007)         |
| THMs                                                                                | 0.71                            | (Chaib and Moschandreas 2008)     |
| THMs, DCAA, TCAA                                                                    | n/a                             | (Ghebremichael et al. 2008)       |
| THMs, HAAs                                                                          | n/a                             | (McBean et al. 2008)              |
| THMs                                                                                | 0.31-0.39                       | (Semerjian et al. 2009)           |
| HAA9                                                                                | n/a                             | (Zhang et al., 2011)              |
| HALs, HKs, THMs, HANs NDMA,<br>HAcAms, HNM, Bromate, Chlorate,<br>Chlorite, Nitrite | Qualitative analysis            | (UK WIR 2014)                     |

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## Chapter 3. Aims and Objectives

The overall aim of this research was to establish operational strategies to simultaneously monitor, predict and minimise the formation of a wide range of both regulated and non-regulated disinfection by-products during water treatment and distribution.

Despite the fact that to-date the occurrence of DBPs has been widely studied during water treatment, there remain knowledge gaps concerning their formation and fate in distribution systems, the collaborative impact of formation parameters and the best disinfection strategies for minimising a broad range of DBPs simultaneously. In addition, water companies lack monitoring and action tools at their disposal to predict and proactively adapt water treatment processes, to minimise the formation of disinfection by-products. As such, a set of research questions has been developed to investigate the key issues in this research area:

- Determine the occurrence, speciation and fate of regulated and unregulated DBPs in full-scale drinking water distribution systems.
- Determine the factors (e.g. water quality parameters; operational parameters) that influence the levels of regulated and unregulated DBPs in distribution systems.
- Assess the performance of Simulated Distribution System (SDS) tests to simultaneously predict the occurrence, speciation and fate of regulated and unregulated DBPs in distribution systems.

In doing so, gain new knowledge regarding the formation and fate of the studied unregulated DBPs (HANs and HAcAms) in distribution systems.

- Assess the impact of potential disinfection practice alteration on the formation of the studied DBPs, i.e. switching from chlorination to chloramination for residual disinfection.

In doing so, gain new knowledge regarding the relative formation of and bromine incorporation into the studied regulated (THMs and HAAs) and unregulated DBPs (HANs and HAcAms) by these two disinfection methods.

- Determine the potential of amide-containing precursors to form regulated and unregulated DBPs, especially the haloacetamides, for which precursor information is lacking.

In the context of this research, ‘unregulated’ DBPs (also referred to as ‘N-DBPs’ in places in this thesis) are limited to haloacetonitriles and haloacetamides. This was based on the knowledge priorities of the sponsoring water company and because of the practical limitations that would have been associated with including several other classes of unregulated DBPs (e.g. nitrosamines), each requiring their own separate sampling and analytical protocol.

With the EU Water Framework Directive, currently effective in the UK, anticipated to already regulate the sum of THMs and projected to include HAAs at specific distribution system locations, information is essentially needed to comprehend the behaviour of these within full-scale systems and devise operational strategies. In addition, the lack of the same information on two groups of nitrogenous DBPs, HANs and HAcAms, suspected of posing higher health concerns than the currently regulated ones, imposed their addition in this research project towards a comprehensive framework on the topic of DBP minimisation.

## Chapter 4. Materials and Methods

This chapter summarises the materials and methodologies that were used to assess and predict the spatial and temporal variability of DBPs, and the impact of potential operational alterations, in four full-scale water treatment works and their distribution systems. In addition, it demonstrates the experimental design followed to evaluate the propensity of amide compounds to act as N-DBPs precursors in drinking water.

### 4.1 DBP occurrence in actual and simulated distribution systems.

For the purposes of this analysis a total of 800 L of drinking water was collected from water treatment works and downstream locations. 480 bottles were filled headspace-free for incubation and approximately 2000 extraction vials were taken to gas chromatography for DBP quantification.

#### 4.1.1 Selection of sampling water works and downstream locations

To-date, it is fairly well understood that the treatment processes implemented in water treatment works have an important role in the subsequent water quality and reactions monitored in distribution systems (UKWIR Ltd. 2014). Therefore, the focus of this study was in the formation of DBPs in distribution systems and not during water treatment processes. As such, the selection of water supply systems to include in this research was mainly based on specific final water characteristics and specifications of the water distribution network. The criteria by which the four water supply systems were selected to obtain fundamental knowledge for the fate of DBPs in distribution were the following:

- Frequent reported formation of moderate to high levels of total THMs ( $> 30 \mu\text{g/L}$ ), from the assessment of historical data (2007-2014) in final waters and storage points.
- Sufficient data availability to run a distribution system hydraulic model to determine water age variation in the networks.
- Inclusion of water treatment works that were applying chlorine or chloramines, of which at least one was presently being considered by the sponsoring water company for disinfection method review or alteration.
- Variation of geographical locations, to include final waters with different bromide levels and NOM patterns.
- Presence of storage locations (reservoirs, water towers etc.) equipped with sampling taps, to facilitate field work in downstream locations.

- Absence of final water blending in distribution with other treatment works or sources of different quality. Also, booster chlorination networks were excluded from the selection.

All four selected water works were assets of Anglian Water Utilities Ltd. (**Table 4.1**), however to preserve confidentiality they are not named in this study, but are referred to as:

**A** WTW: Uses free chlorine as disinfectant and includes a large network (~ 1,150.8 km) with various water ages.

**B** WTW: Uses free chlorine as disinfectant, has a medium network (~ 700 km) but is characterised by more areas with high water ages.

**C** WTW: Uses chloramination as a disinfection method in distribution, and has a large (~ 6,140 km) and complex network.

**D** WTW: In line chloramines are applied in a small network (~ 265 km), but unlike the other three, that have similar treatment processes, this one performs slow sand filtration.

Below in Table 3.1 a detailed description of each water treatment works and its characteristics is provided. Within each distribution system, three downstream locations (reservoirs, water towers, taps) were chosen for sampling, to represent the various water ages determined from the water age modelling. The modelling software package used was SynerGEE v4.6.0, a propriety software provided by DNVGL (Norway), which also produces modelling packages for gas, oil and electricity distribution. The models were built from the water utility GIS data and billing records, which were then calibrated against telemetry data and field pressure logging to build a representative simulation of the water distribution network, with all details of pumps, storage (towers and reservoirs), pressure regulators and mains. The hydraulic simulations were solved using the Darcy-Weisbach equations. The prediction of water age required the continuous run of simulations until stable water age values were calculated by the model, which lead to the generation of maps with coloured elements according to the water ages (**Appendix F**).

**Table 4.1:** Specifications of selected water treatment works for distribution system monitoring.

| <b>Water Works<br/>(WTW)</b> | <b>Source<br/>water</b> | <b>Pre-oxidant</b> | <b>Treatment processes</b>                                    | <b>Final disinfectant</b> | <b>Bromide <sup>a</sup><br/>[µg/L] - <i>median</i></b> | <b>Total THMs <sup>b</sup><br/>[µg/L] - <i>median</i></b> | <b>Network size<br/>[m]</b> | <b>Water Age<br/>[hours]</b> |
|------------------------------|-------------------------|--------------------|---------------------------------------------------------------|---------------------------|--------------------------------------------------------|-----------------------------------------------------------|-----------------------------|------------------------------|
| <b>A</b>                     | SW                      | Ozone              | Clarification, filtration,<br>GAC, chlorination               | Chlorine                  | (10-45) – 21.2                                         | (6-82) – 27.6                                             | 1,150,800                   | 6 - >144                     |
| <b>B</b>                     | SW                      | Ozone              | Clarification, filtration,<br>GAC, chlorination               | Chlorine                  | (9.4-48.1) – 25.85                                     | (5-72) – 26.6                                             | 698,700                     | 6 - >106                     |
| <b>C</b>                     | SW                      | Ozone              | Clarification, filtration, GAC,<br>chlorination, ammonisation | Chloramine                | (75.7-135) – 97.05                                     | (5-75) – 32.5                                             | 6,140,000                   | 6 - >144                     |
| <b>D</b>                     | SW                      | n/a                | Slow sand filtration, aeration<br>chlorination, ammonisation  | Chloramine                | (14.5-40.6) – 23.4                                     | (14-45) – 26.4                                            | 264,000                     | 6 - >72                      |

a. Historical data from 2007-2014 (final water).

b. Historical data of distribution network from 2007-2014.

### 4.1.2 Sample collection, preservation and storage

To address the spatial and seasonal variation of DBPs in distribution systems, 4 water treatment works and 12 downstream locations were sampled in four rounds during a period of one year (September 2015 – September 2016). The same sampling collection, preservation and storage was performed during all sampling rounds to the selected water treatment works and downstream locations. The annual sampling schedule is presented for reference in **Table 4.2**.

**Table 4.2:** The sampling rounds schedule for each water treatment works (WTW).

| Sampling round | WTW  | Month – Year   |
|----------------|------|----------------|
| <b>Round 1</b> | A, B | September 2015 |
|                | C, D | October 2015   |
| <b>Round 2</b> | A, B | February 2016  |
|                | C, D | March 2016     |
| <b>Round 3</b> | A, B | May 2016       |
|                | C, D | June 2016      |
| <b>Round 4</b> | A, B | August 2016    |
|                | C, D | September 2016 |

#### 4.1.2.1 Sample collection

During most of the sampling rounds, two sets of water samples were taken from the water treatment works; filtered non-disinfected water and final disinfected water. Following the sampling in the works, another set of samples was collected from the 3 selected downstream locations. The former was used to perform Simulated Distribution System (SDS) tests (described below) and the latter was analysed directly as actual distribution samples. All glassware used for sampling were prepared and cleaned according to Appendix A-Table A.1: *Preparation of sample & analysis containers*.

##### 4.1.2.1.1 Water treatment works sampling

In the chlorinated treatment works (A&B), 30 L of filtered water was collected prior to disinfection from each works. These were placed in clean 5 L amber glass bottles with PBT (Polybutylene Terephthalate) screw caps with PTFE (Teflon) protected seal and stored in coolers with ice packs for transportation to the lab. In the chloraminated treatment works (C&D), 15 L of disinfected water was collected in Winchester amber bottles of 1 L and were treated as SDS test samples from the time of the sampling. Thus, they were not stored in the coolers but were left at ambient temperature until their quenching on the selected time intervals in the AW facilities or incubation in the lab. Another 15 L were collected prior to disinfection, in

larger containers that were preserved with ice packs until their storage in the lab. After sampling, any spillage was cleaned away to leave the sampling area clean and dry, for health and safety reasons. All samples were labelled clearly with a specified coding of each sampling location.

#### **4.1.2.1.2 Actual distribution system samples**

Sampling was also conducted from the selected downstream locations of each water treatment works, to be compared with the results of the simulated distribution system tests during all sampling rounds. Since these sampling taps were not all routinely used, it was necessary to flush the system for several minutes (3-5 minutes) to obtain consistent samples. All samples were collected in duplicate in two separate amber glass bottles (1L) at the same time under identical conditions and treated the same during field and laboratory procedures. Sampling bottles were filled to the top and then were de-chlorinated or de-chloraminated (based on the disinfection method applied in the system) with the selected quenching agents (ammonium chloride and ascorbic acid, see Chapter 4.2.2.2) *in situ*, to eliminate further reactions taking place before analysis. The actual distribution samples were immediately stored in coolers in low temperature (-6°C) and to avoid direct sunlight, for short-term storage during onward delivery to the laboratory in Imperial College. The samples were transported and stored in the lab within maximum 12 hours.

During field work data for several water quality parameters were also collected from the online monitoring systems in the downstream locations, such as water temperature, TOC measurement, UV absorbance, pH and chlorine residual. When online measurements were not available, field thermometers and chlorine test kits (Pocket Colorimeter™ II, Hach, UK) were used to determine the experimental conditions.

#### **4.1.2.2 Sample preservation and storage**

The nature of the experimental design (time interval analysis) and the long list of DBP analytes to be quantified imposed the necessity to introduce appropriate quenching agents in the samples. The role of the addition of dry salts was to eliminate the disinfectant residual from the samples and thus cease any further reactions between the disinfectant and the NOM. There is no universal quenching agent, so the selection was based upon their reported ability to ensure stability of the selected analytes according to the disinfection method implemented in the supply systems. Previous stability tests had shown that quenching agents would not adversely affect the stability of THMs and HAAs, however this was not the case for HANs and HAcAms (Singer et al. 2002; Liew et al. 2012; Kristiana et al. 2014). Therefore, for the determination of THMs, HAAs, HANs, it was decided that the most appropriate quenching agent in chlorinated samples

would be ammonium chloride and in chloraminated samples would be ascorbic acid, in concentrations of 100 mg/L and 50 mg/L, respectively (Munch and Hautman 1995; Liew et al. 2012). Upon quenching, dechlor(am)inated samples, either from distribution or SDS tests, were stored in the Roger Perry Laboratory fridge at 4°C until further analysis. The dechlorinated and dechloraminated samples were then extracted within maximum 24 hours.

#### **4.1.3 Preparation of disinfectant solutions and disinfectant dosing**

Chlorine stock solution was prepared by the addition of 100 mL of concentrated sodium hypochlorite solution (NaClO) in 500 mL of ultrapure water. This solution was placed in the refrigerator at 4°C and was used to prepare fresh diluted chlorine solutions (~0.25M) for spiking during the whole experimental period, though it was necessary to measure the concentration before each experiment to account for chlorine decay over time. Monochloramine solutions were prepared with controlled addition under mixing of chlorine solution to an ammonia solution (N/Cl molar ratio: 1.4/1), checked to be alkaline (pH 8), so that monochloramine was the predominant species. The ammonia solution (0.12M) was prepared in a volumetric flask of 250 mL, with the addition of 1.61 g of ammonium chloride (NH<sub>4</sub>Cl) and phosphate buffer of pH 8 at 10 mM. The monochloramine solution (0.1M) was left in the dark and then was titrated to check the concentration and ensure that limited free chlorine was present.

Chlorine and chloramine concentrations were measured by DPD-FAS titration method 4500-Cl F that can be found in the Standard Methods for the examination of water and wastewater (APHA, WEF, and AWWA 1999). In this method, N, N-diethyl-p-phenylenediamine (DPD) is used as an indicator in the titrimetric method with ferrous ammonium sulphate (FAS). This method involves the preparation of three solutions to measure chlorine (*Appendix A.2*): phosphate buffer solution, DBP indicator solution and the FAS titrant, whereas to measure monochloramine a fourth one of potassium iodide was also necessary. The titration procedure followed the steps below:

- i. 100 mL of the unknown disinfectant concentration solution was added in a conical flask.
- ii. 5 mL of the phosphate buffer was added in the solution with a pipette.
- iii. 5 mL of the DPD indicator solution was added in the solution (*if chlorine was present the solution would become pink*)
- iv. FAS titrant is then added in the solution dropwise from a burette until the indicator is consumed and the solution becomes transparent.

- v. The amount of the FAS titrant used to consume the indicator is equal to the concentration of chlorine in the sample as  $\text{Cl}_2/\text{L}$ .

For monochloramine concentration determination, a few drops (2-3) of potassium iodide were added in the sample after the completion of the above steps, to ensure that the presence of chlorine was limited ( $< 0.1\text{mg/L}$ ). This would colour again the sample and steps iv-v were repeated to estimate this time the concentration of monochloramine. This procedure was used multiple times during the experiments not only to verify the concentration of the disinfectant stock solutions and check their stability, but also to determine the disinfectant dosing in the following tests and measure the residual in the samples.

The water quality diversity of the selected water treatment works and the annual distribution of the sampling meant that the collected water matrices would present different characteristics and organic content, therefore their disinfectant demand was expected to vary somewhat between the seasonal rounds. Thus, prior to any spiking in the lab, the DPD ferrous titration was also performed to determine the amount of disinfectant to be injected in the samples to simulate the residual disinfectant observed in finished water when leaving the actual water treatment plants. This residual disinfectant would vary between  $0.9\text{-}1.3\text{ mg/L}$  during all sampling rounds and treatment works.

## 4.2 Experimental design of Simulated Distribution System (SDS) tests

The simulated distribution system (SDS) test is a bench scale technique that involves incubating water samples at simulated distribution conditions (i.e. disinfectant residuals, temperatures, water ages) to predict the formation of DBPs within distribution (APHA 1999). The following laboratory apparatus and reagents were used to prepare the SDS samples.

**Table 4.3:** Apparatus and reagents for SDS tests.

| Apparatus               | Characteristics                      |
|-------------------------|--------------------------------------|
| Amber glass bottles     | Winchester bottles of 1000 mL        |
| Caps, PTFE-faced septa  |                                      |
| Pipette (1)             | Eppendorf Research® plus 100-1000 µL |
| Pipette (2)             | Eppendorf Research® plus 20-200 µL   |
| Incubator               |                                      |
| Stir plate              |                                      |
| Stir bar magnet         |                                      |
| Tweezers                |                                      |
| Reagents                |                                      |
| Chlorine solution       | Disinfectant (0.25 M)                |
| Monochloramine solution | Disinfectant (0.1 M)                 |

Before the disinfectant dosing and the preparation of the SDS samples, stored collected water were left outside the fridge or incubated to reach the same temperature as the one noted during sampling in the treatment works, to simulate the temperature conditions during actual disinfection. For the water samples used for the SDS tests, fresh chlorine solution and monochloramine solution were prepared from the stock solutions, with concentrations of these oxidants determined and monitored by DPD-FAS titration. The preparation of the SDS tests is summarised in the following steps:

- Each bottle was rinsed with the collected treated but non-disinfected water sample which was then discarded, to achieve sample homogeneity.
- Then each bottle was filled approximately 2/3 (~750 mL) with the non-disinfected water sample.
- With the aid of tweezers, a stir bar magnet was introduced in the bottle and was transferred on a stir plate (set on low-medium stir speed), to prevent localised areas of disinfectant during the spiking.
- The water sample was spiked with pre-determined volume of chlorine or chloramine solution, to achieve the same residual disinfectant concentration as in the actual treatment plant on the sampling day.

- v. The SDS bottle was taken off the stirrer and was filled up to the top until (avoid overflowing) until the water-air interface becomes convex.
- vi. The bottles were capped headspace free, inverted to mix and checked for trapped air bubbles. If air bubbles were present, the bottle was refilled until no air was observed in the SDS samples, to safeguard the detection of the volatile compounds.
- vii. Finally, the SDS bottles were stored in the incubator at the on-site measured temperature and contact time that was selected to simulate the water ages in distribution.

After the completion of the incubation time, the samples were quenched in accordance with the agent selected for the disinfection method applied and stored in the refrigerator until their further analysis. The SDS samples were analysed subsequently for residual disinfectant, pH, UV absorbance, TOC, and DBPs.

## **4.3 Other water quality analyses**

### **4.3.1 Residual disinfectant analysis**

All water samples, prior to their fortification with the quenching agents, were firstly analysed to determine the amount of residual chlorine or chloramine. This had to be a careful and rapid procedure since it was necessary to limit loss of the volatile DBPs from the samples and accurate measurement of the residual amount of disinfectant. The process of measuring the residual disinfectant in the samples was the same one implemented to determine the initial disinfectant dosing; DPD Ferrous titrimetric method (*4500-Cl F*) (APHA 1999), that can be found in detail in *Chapter 4.1.3*. An active residual of >0.2 mg/L had to be present in the SDS samples for the test to be considered valid before their quenching, since 0.2 mg/L is the minimum disinfection requirement set by US EPA (2010) to ensure pathogen inactivation in drinking water distribution (in at least 95% of the downstream locations).

### **4.3.2 Total Organic Carbon (TOC) analysis**

Total organic carbon was measured as non-purgeable organic carbon (NPOC) on a Shimadzu TOC-V instrument via a UV/persulphate oxidation method in Imperial College, with several analyses performed on a Shimadzu TOC- V<sub>CSH</sub> in Brunel University via combustion catalytic oxidation/ NDIR. For the purpose of TOC analysis, water samples were filtered with pre-combusted GF/F filters (Whatman, UK) to remove possible suspended solids, and acidified with hydrochloric acid (HCl) to pH 2 for preservation, prior to storage at 4°C for a maximum of 20 days. The instrument was calibrated in each analysis with the use of freshly prepared TOC standards and each sample was analysed in duplicate. The method detection limits (MDL) for NPOC ranged between 0.06 and 1.0 mg/L, during the whole analysis period and was determined by a simultaneous run of five blank sample replicates in which MDL was three times the standard deviation. Since the number of samples to be analysed each time was high, blank samples were introduced in the run in every 15 samples to ensure the instrument sensitivity and a 10 mg/L standard was tested in the beginning and end of the run for quality control.

### **4.3.3 UV absorbance and Specific UV absorbance (SUVA)**

UV absorbance (UV<sub>254</sub>) and a calculated parameter known as specific UV absorbance (SUVA) both gave a relative indication of the hydrophilic or hydrophobic nature of the water matrices. Therefore, they have been included in several DBP studies, to investigate any correlation with DBP formation and to understand the impact of different organic constituents.

UV absorbance was measured in the lab in a Camspec M550/1 double beam scanning UV/visible spectrophotometer which induced electron stimulation of the valence layer. Subsequently, Specific UV absorbance is usually calculated by dividing DOC measurement from UV absorbance value at 254 nm and is an indicator of the humic content in water. However, in our case since the sampling took place at the end of the treatment works where the dissolved organic carbon (DOC) measurement is expected to be the measurement of total organic carbon (NPOC), SUVA was calculated by dividing NPOC instead. So, the following equation was used to calculate SUVA in our samples:

$$\text{SUVA} = (\text{UVA} [\text{cm}^{-1}] / \text{TOC} [\text{mg/L}]) \cdot 100 [\text{cm} \cdot \text{m}^{-1}] \quad \text{Equation 4.1}$$

## 4.4 Investigation of amides as N-DBP precursors

Amides, abundant in surface waters and sediments, consist of a substantial ratio of dissolved organic nitrogen (DON), and represent around 2-3% of total natural organic matter (NOM) (Thurman 1985; Świetlik et al. 2004). Amides are also present in around 25% of pharmaceuticals and other medically important compounds (Ghose et al. 1999), which nowadays have been incorporated in trace concentrations in the water cycle and is likely to reach the water treatment works (WHO 2011a; Bull 2014).

Chapter 5 reports on a set of experiments aimed to assess the relative effect of six model amide precursor compounds in the formation of N-DBPs (HAcAms and HANs), HAAs and THMs, upon chlorination and chloramination. The methodology of this study is presented in detail in the following subchapters and involved controlled laboratory tests under various pH, bromide dose and incubation time conditions.

### 4.4.1 Selection of amide model compounds

The selection of the amides was based in the following parameters; their functional group, structure, molar mass, their previous reported DBP formation potential and their hydrophilicity. The six selected amides were the following:

*Acetamide* (IUPAC: ethanamide) belongs in the wide group of carboxamides and it is the simplest amide derived from acetic acid. This model compound has been previously reported to have a formation potential for THMs and HAAs of 1 and 5  $\mu\text{g mg C}^{-1}$ , respectively (Bond et al. 2009, 2012), whereas it has shown formation potential for N-DBPs (DCAN, TCAN and TCNM) of 0.4 % M/M (Bond et al. 2009).

*Acetoacetamide* contains a beta-dicarbonyl group, which is known to act as a reactive THM and HAA precursor structure (Dickenson et al. 2008). Therefore, it was hypothesised that this compound is also a potential HAcAm precursor.

*Polyacrylamide* is a polymeric coagulant aid used in water treatment processes which would be interesting to investigate whether its presence in treated water can function as a DBP precursor, regardless of the NOM characterisation. Despite the fact that about 95% of the polymers are being absorbed in the flocculation particles during water treatment, a 5% remains dissolved in the water and may be spread in surface and ground waters (Guzzo and Guezennec 2015). In addition, a recent precursor study investigated the potential of polyacrylamide to inhibit nitrosamines and THMs formation during chloramination and concluded that even though THMs seemed unaffected, the application of polyacrylamide promoted the formation of nitrosamines (Li et al. 2017). Even though, the absence of nucleophilic sites in the structure of

polyacrylamide suggests relative inertness, its susceptibility to multiple degradation pathways is high; the amide group can undergo hydrolysis or dehydration (Caulfield et al. 2003). The degradation of polyacrylamide may contribute to the release of acrylamide, a compound of health concern and this is why it was also included in this analysis as the fourth model compound.

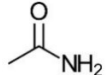
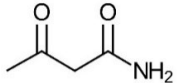
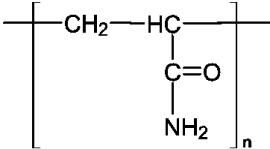
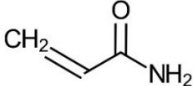
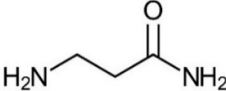
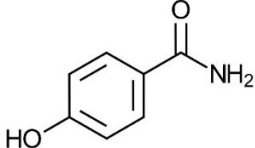
*Acrylamide* is the monomer used in the production of polyacrylamide and is known to be found as a residual in water treatment works, readily mobile in aqueous environments and highly leachable in soil (WHO 2004). Acrylamide was previously detected in concentrations of  $<5 \mu\text{g/L}$  in river and tap water samples in the US (WHO 2004), with significant lower levels of  $\mu\text{g/L}$  reported in the UK. Both acrylamide and polyacrylamide apart from being used in water and wastewater treatment have been reported as grouting agents in the construction of drinking water reservoirs and wells (IPCS and WHO 1985), that suggests their widespread occurrence in water resources. In addition, acrylamide contains two primary functional groups, amide and vinylic carbon-carbon double bond, therefore is susceptible to nucleophilic reactions and presents high chances to act as a precursor for DBPs.

*$\beta$ -Alaninamide* is an amide that derives from the relative amino acid,  $\beta$ -Alanine acid known of generating significant yields of THMs and HANs (Hu et al. 2010). No information about the natural occurrence of this compound was found in the readily-available literature. However, the structural configuration of this compound that includes a carbonyl bonded with a highly reactive amino radical, may promote the formation of N-DBPs in water samples.

*Hydroxybenzamide (4-hydroxybenzamide)* was selected as the aromatic moiety of the study as aromatic precursors have been previously shown high N-DBP formation potentials (Le Roux et al. 2016).

This study reported values for slightly hydrophobic ( $\log K_{ow} < 0.5$  to highly hydrophilic ( $\log K_{ow} = -1.8$ ) substances. The above model compounds were commercially available at lab-grade purity from Sigma-Aldrich and Fintech industry. In the following table (Table 4.4), the structures, molar masses,  $\log K_{ow}$  and the predicted fractions of the proposed model compounds are being summarised. All selected model compounds belong in the wider functional group of amides.

**Table 4.4:** Selected amide model compounds for the haloacetamide precursor study.

| Name               | Structure                                                                           | Molecular Weight [g/mol] | Log K <sub>ow</sub> (and predicted fraction) |
|--------------------|-------------------------------------------------------------------------------------|--------------------------|----------------------------------------------|
| Acetamide          |    | 60                       | -1.26 ( <i>hydrophilic</i> )                 |
| Acetoacetamide     |    | 101.1                    | -1.15 ( <i>hydrophilic</i> )                 |
| Polyacrylamide     |    | 5,000,000-6,000,000      | n/a                                          |
| Acrylamide         |    | 71.0                     | -0.7 ( <i>hydrophilic</i> )                  |
| β-Alaninamide      |   | 88.1                     | -1.81 ( <i>hydrophilic</i> )                 |
| 4-Hydroxybenzamide |  | 137.14                   | 0.3 ( <i>slightly hydrophobic</i> )          |

#### 4.4.2 Reagents and sample preparation

The experimental plan of this work package was designed to be conducted in two phases; the *screening* and the *detailed* phase. During the *screening phase*, all selected amide model compounds were tested primarily for N-DBPs (haloacetamides and haloacetonitriles), but also for THMs and HAAs formation potential during both chlorination and chloramination at pH 8 and after 24 hours of incubation with the absence of bromide. Whilst all classes of DBPs were identified during the screening phase, it was decided to design a *detailed phase* which included more experimental variables and provided an improved understanding of the N-DBP formation from amides. During the detailed phase, the six selected amides were chlorinated and chloraminated in both pH 7 and 8, for 4 and 24 hours and with and without the presence of bromide. The experimental design plan for both phases is summarised in **Table 4.5**.

**Table 4.5:** Experimental design for amide precursor study (*screening and detailed phase*)

| Experimental phases | Disinfection |            | Water age |      | pH |   | Bromide [ $\mu\text{g/L}$ ] |     |
|---------------------|--------------|------------|-----------|------|----|---|-----------------------------|-----|
|                     | Chlorine     | Chloramine | 4 h       | 24 h | 7  | 8 | 0                           | 100 |
| <b>Screening</b>    | ✓            | ✓          | -         | ✓    | -  | ✓ | ✓                           | -   |
| <b>Detailed</b>     | ✓            | ✓          | ✓         | ✓    | ✓  | ✓ | ✓                           | ✓   |

Prior to sample preparation, several solutions were prepared to control the pH and oxidation of the samples. So, sodium phosphate buffers of 10 mM at pH 7 and 8 were prepared by mixing monobasic and dibasic stock solutions (*Appendix A. Supplementary Information*) and served as the basis in which amides were spiked. Chlorine and chloramine solutions, of 0.25 M and 0.1 M respectively, were prepared as described in *Chapter 4.1.3* and measured by DPD-FAS titration (APHA 1999) in minimum triplicate samples on the day of sample preparation. Finally, all amide stock solutions were prepared in a concentration of 1 M to facilitate further dilutions, by adding the appropriate amount in grams to 100 mL volumetric flasks (according to their molecular weight).

For the sample preparation, 250 mL (*nominal volume: 280 mL*) amber glass vials with PTFE lined screw caps were filled up to 2/3 (~200 mL) with 10 mM of each phosphate buffer. The bottles were then transferred in a stirrer apparatus where they were fortified with the predetermined volume of amide stock solution of 28  $\mu\text{L}$  to achieve a final concentration for each amide of 10  $\mu\text{M}$ . Following that, when addition of bromide was in the experimental plan, 28  $\mu\text{L}$  of a bromide stock solution was added to achieve a

concentration of 100 µg/L. Next, either chlorine or chloramine was added at a formation potential dose of 20 M/M. After the completion of the above steps, the sample bottles were filled to the top with the relative phosphate buffer and capped headspace free before their incubation of 4 or 24 hours. When the selected incubation times were completed the samples were quenched with the appropriate quenching agents (Chapter 4.1.2.2) to remove any residual disinfectant and preserve the DBPs formed, and were extracted immediately. All samples were prepared in duplicates in different bottles to calculate standard deviations and identify errors. When the extracted samples were processed and their DBP concentrations were identified, these were divided by the molecular weight of each DBP species to facilitate comparisons in %M/M. For the purpose of this study, approximately 240 samples were extracted and analysed for HAcAms, HANs, HAAs and THMs.

## 4.5 DBP analyses

Disinfection by product analysis commences when the selected incubation time of the water samples was completed and was divided into two different phases: extraction and chromatographic analysis. The determination of all target disinfection by-products in this study was performed by liquid-liquid extraction (LLE) and gas chromatography coupled with electron captured detection (*GC-ECD*), using two separate methods; a modified EPA Method 551.1 (for *THMs*, *HANs* and *HAcAms*) and EPA Method 552.3 (for *HAAs*). These methods have been widely implemented to identify the selected DBPs from water samples, and have been modified to improve the sensitivity, selectivity, credibility, accuracy and repeatability of this analysis. A detailed methodology of the two DBP analysis phases can be found in the following subchapters; Extraction (*Chapter 4.5.1*) and Chromatographic analysis (*Chapter 4.5.2*).

### 4.5.1 Extraction of DBPs from water samples

During the extraction phase an amount of sample aliquot (30 and 40 mL, in method 551.1 and 552.3, respectively) was acidified to ensure DBP stability, followed by the addition of salts (sodium sulphate and copper II sulphate pentahydrate), to increase the ionic strength of the aqueous phase and thus later drive the targeted compounds into the organic phase. Then, an organic solvent was added (3 and 4 mL of MTBE, in method 551.1 and 552.3, respectively) and mixed into the water samples, to complete the displacement of target organic halogens between the two phases. The salt addition also decreases the solubility of the organic solvent in the aqueous phase to allow higher volumetric recovery. By shaking the layers, the contact area between the two phases is increased, thus the target compounds are moved to the phase in which they are most soluble; the non-polar. This organic phase was then analysed by gas chromatography electron capture detection (*GC-ECD*). Prior to extraction, all samples were quenched to remove any residual chlorine and chloramines with the selected preservative salts, as discussed previously. Then water samples were either immediately extracted or stored for a maximum of 24 hours at 4°C. All extractions were performed in Roger Perry Laboratory at Imperial College.

#### 4.5.1.1 Extraction for THMs and N-DBPs (Method 551.1)

The analysis of four trihalomethanes (*THMs*), seven haloacetonitriles (*HANs*) and eight haloacetamides (*HAcAms*) began with liquid-liquid extraction from the water samples based on EPA Method 551.1 (Munch and Hautman 1995; Hautman and Munch 1997). The same procedure was followed for the

extraction of these compounds in both the SDS tests and amide precursors tests. The extraction procedure took approximately two hours for 12 samples.

The following laboratory appliances and reagents were used to extract THMs, HANs and HAcAms from the water samples (Table 4.6-4.7). The analytical standards, containing THMs (Supelco 48045) and 4 HANs (BCAN, DCAN, DBAN, TCAN) (Supelco 48046) were available as mixtures by Sigma Aldrich (UK), whereas the rest of the HANs were supplied separately by Toronto Research Chemical Inc. (DBCAN) or Sigma-Aldrich (MCAN, MBAN). The HAcAms were individually supplied by Orchid Cellmark (BCAcAm, DBAcAm, BDCAcAm, TBAcAm, DBCAcAm), Alfa Aesar (DCAcAm, TCAcAm) and Sigma-Aldrich (MCAcAm, MBAcAm). The initial intention was to quantify 9 HANs, however two species (BDCAN, TBAN) were excluded due to the difficulty in obtaining the analytical standards. All the chemicals used, including quenching agents, extraction salts, extraction solvent, and internal standards, were obtained at high purity (analytical grade) from Sigma Aldrich or VWR International while all solutions were prepared in ultra-pure water treated via reversed osmosis (RO water).

**Table 4.6:** Required laboratory tools and apparatus for the extraction Method 551.1.

| Apparatus                            | Characteristics                                |
|--------------------------------------|------------------------------------------------|
| Extraction glass containers          | Kimble® 60958A-16 clear 60mL                   |
| Caps, PTFE-faced septa               | Kimble #73802-24400                            |
| Extraction vials holder              | Metallic - 24 places                           |
| Standard solution storage containers | 30 mL, amber glass bottles with TFE-lined caps |
| Laboratory scale                     | Metler Toledo XP1203S (max 1210 g)             |
| Weighting boats                      | Diamond shaped - 80 mm × 60 mm × 14 mm         |
| Stainless spatula                    |                                                |
| Pipette (1)                          | Eppendorf Research® plus 100-1000 µL           |
| Pipette (2)                          | Eppendorf Research® plus 20-200 µL             |
| Pasteur pipette                      | VWR Int. - 150 mm                              |
| pH indicator strips                  | pH range 2-10                                  |
| Bottle Top Dispenser                 | (0-5 mL)                                       |
| Autosampler vials                    | Thermo Scientific™ 11mm Clear Glass Crimp Top  |
| Autosampler caps                     | Teflon-faced septa                             |

**Table 4.7:** Reagents and standards used for extraction Method 551.1.

| Reagents                                                              | Uses                 |
|-----------------------------------------------------------------------|----------------------|
| Reagent water                                                         | Solvent & cleaning   |
| Methyl tert-butyl ether (MTBE)                                        | Extraction solvent   |
| 1-Bromo-4-fluorobenzene                                               | Internal standard    |
| Sodium Sulfate (Na <sub>2</sub> SO <sub>4</sub> )                     | Extraction salt      |
| Copper II sulfate pentahydrate (CuSO <sub>4</sub> ·5H <sub>2</sub> O) | Extraction salt      |
| Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )                       | Acidifier            |
| DBP Stock standard solutions                                          | Analytical standards |

The method required the preparation of three main solutions, with the aid of the above reagents, to be used during the steps of the extraction process. The first one was the pH adjustment solution by diluting multiple times concentrated sulphuric acid into RO water, to achieve a molar concentration of 0.1M (-0.2N). The second solution was the extraction solvent (MTBE) that had to be fortified with the internal standard (1-Bromo-4-fluorobenzene). The final concentration of 1-Bromo-4-fluorobenzene in MTBE was 1 µg/mL and the solution was stored in a glass container capped with a volume dispenser in the freezer (-18°C). The final was that of the analytical standards, a mixture of the target compounds that were introduced into RO water samples and extracted to facilitate instrument calibration and analytical quality control. These solutions were prepared from concentrated stock solutions (2000 µg/mL) diluted initially in high purity acetone and then RO water, with a concentration of 1200 µg/L, to enable further calibration dilutions.

The extracted samples were then either introduced immediately to the chromatograph or were stored in the freezer at -18°C. The maximum storage time for the extracted samples of Method 551.1 was 14 days. Those that were not analysed within this time frame were discarded and are not included in the results.

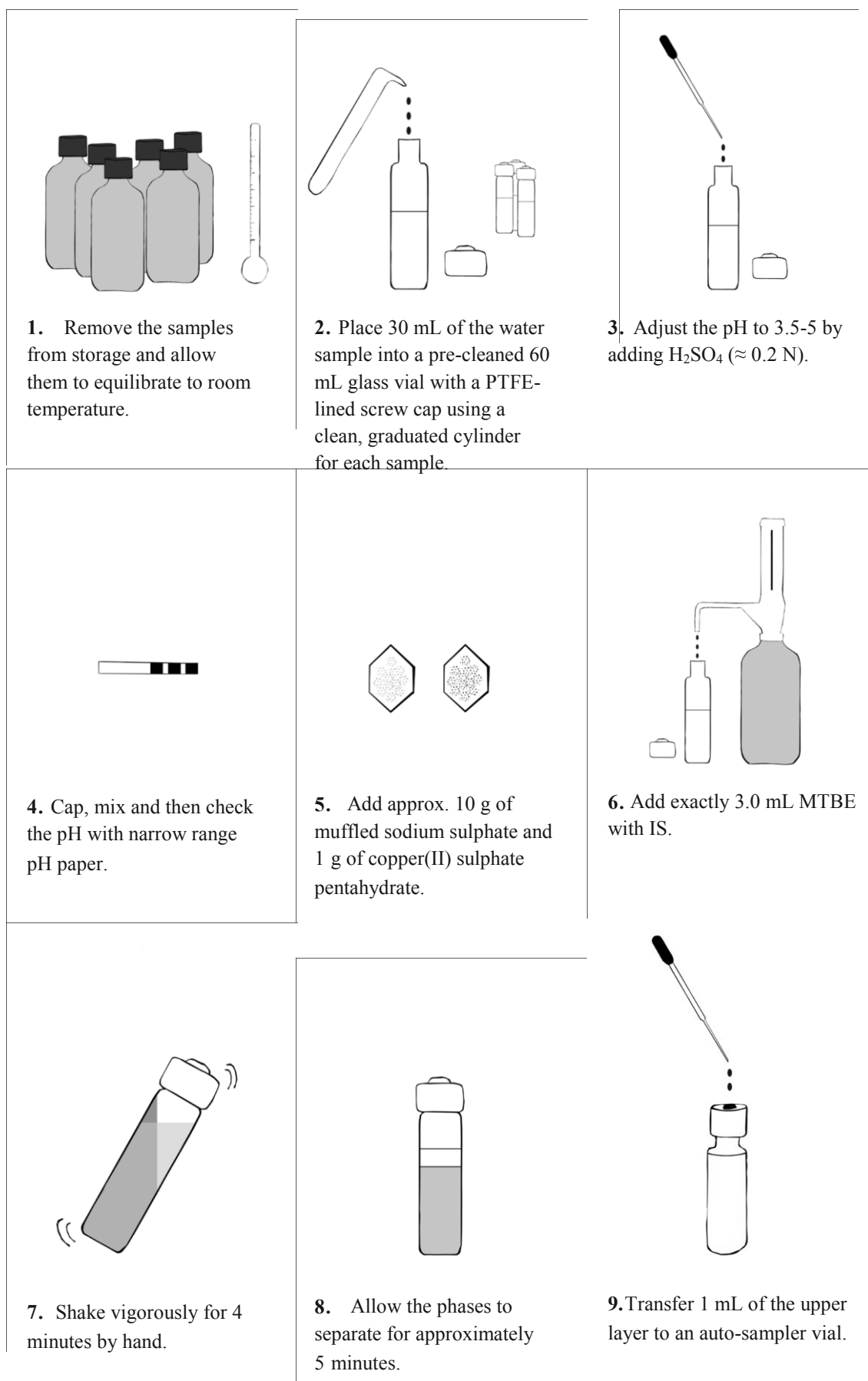


**Figure 4.1:** Illustrated methodology of THMs, HANs and HAcAms extraction (extraction method EPA 551.1).

#### 4.5.1.2 Extraction of haloacetic acids (HAAs)

The analysis of nine haloacetic acids (HAAs) follows a more demanding and time consuming extraction method, EPA Method 552.3 (Domino et al. 2003). Even though it initially follows similar steps as the method analysed previously, a key step is the conversion of haloacetic acids into their respective methyl esters that can be further detected. The same method was followed for the analysis of these compounds in both SDS tests and amide precursors tests. The extraction procedure of these compounds was estimated to be approximately 5 hours for 12 samples.

The following laboratory appliances and reagents were used to extract the nine brominated and chlorinated haloacetic acids (HAAs) from the water samples (Table 4.8-4.9). The analytical standards containing HAAs (Supelco 49107-U) were available as mixture by Sigma Aldrich (UK). All the chemicals used, including extraction salts, extraction solvent, and internal standard were obtained at high purity (analytical grade  $\geq 99.0\%$  or more) from Sigma Aldrich or VWR International while all solutions were prepared in high purity methanol and ultra-pure water treated via reversed osmosis (RO water).

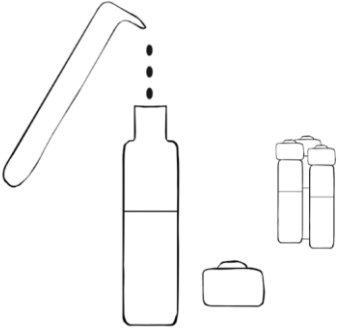
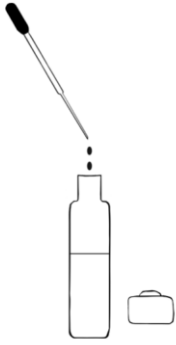
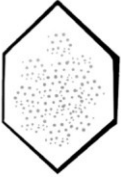
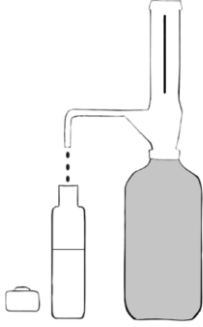
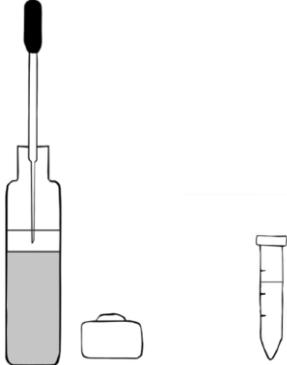
**Table 4.8:** Required laboratory tools and apparatus for the extraction Method 552.3.

| Apparatus                                   | Characteristics                                |
|---------------------------------------------|------------------------------------------------|
| Extraction glass containers                 | Kimble® 60958A-16 clear 60mL                   |
| Caps, PTFE-faced septa                      | Kimble #73802-24400                            |
| Extraction vials holder (24 places)         | Metallic - 24 places                           |
| Laboratory balance                          | 30 mL, amber glass bottles with TFE-lined caps |
| Weighting boats                             |                                                |
| Stainless spatula                           | Diamond shaped - 80 mm × 60 mm × 14 mm         |
| Water bath                                  |                                                |
| Temperature regulator for water bath        |                                                |
| Pipette (1)                                 | Eppendorf Research® plus 100-1000 µL           |
| Pipette (2)                                 | Eppendorf Research® plus 20-200 µL             |
| Pasteur pipette                             | VWR Int. - 150 mm                              |
| Glass pipette                               |                                                |
| Pipette filler                              |                                                |
| pH strips                                   | pH range: 0 - 2.5                              |
| Bottle Top Dispenser                        | (0-5 mL)                                       |
| Graduated centrifugal tubes with screw caps | (15 mL)                                        |
| Centrifugal tubes holder                    | Plastic – 50 places                            |
| Vortex mixer                                |                                                |
| Bottle Top Dispenser                        | (0-5 mL)                                       |
| Autosampler vials                           | Thermo Scientific™ 11mm Clear Glass Crimp Top  |
| Autosampler caps                            | Teflon-faced septa                             |

**Table 4.9:** Reagents and standards used for extraction Method 552.3.

| Reagents                                     | Uses                       |
|----------------------------------------------|----------------------------|
| Reagent water                                | Solvent & cleaning         |
| Methyl tert-butyl ether (MTBE)               | Extraction solvent         |
| 1,2,3-trichloropropane                       | Internal standard          |
| Sodium Sulphate ( $\text{Na}_2\text{SO}_4$ ) | Extraction salt            |
| Sulfuric acid ( $\text{H}_2\text{SO}_4$ )    | Used in multiple solutions |
| Sodium Bicarbonate ( $\text{NaHCO}_3$ )      | Neutraliser                |
| Stock standard solutions                     | Analytical standards       |

The method required the preparation of five solutions, with the aid of the above reagents, to be used during the steps of the extraction and methylation process of HAAs. The first solution was the extraction solvent (MTBE) that had to be fortified with the internal standard (1, 2, 3-trichloropropane). The final concentration of 1, 2, 3-trichloropropane in MTBE was  $1\mu\text{g/mL}$  and the solution was stored in a glass container capped with a volumetric dispenser in the freezer ( $-18^\circ\text{C}$ ). Prior the methylation step, a 10% of sulphuric acid in methanol solution was added in the samples. This was prepared by the addition of 10 mL of sulphuric acid dropwise (due to heat evolution) to 50-60 mL of methanol contained in a 100-mL volumetric flask that was placed in a cooling bath. This was left to cool to room temperature, and diluted to the volumetric mark with methanol. The third solution was an aqueous solution of sodium sulphate in reagent water at a concentration of 150 g/L. Furthermore, a saturated sodium bicarbonate solution was prepared with the addition of this salt into a volume of water, while mixing periodically until the solution had a small amount of undissolved salt. The final solution(s) in this method is the mixture of target analytical standards diluted in water to a concentration of  $1200\mu\text{g/L}$ .

|                                                                                                                                                                                       |                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  <p><b>1.</b> Remove the samples from storage and allow them to equilibrate to room temperature.</p> |  <p><b>2.</b> Place 40 mL of the water sample into a pre-cleaned 60 mL glass vial with a PTFE-lined screw cap using a clean, graduated cylinder for each sample.</p> |  <p><b>3.</b> Adjust the pH to less than or equal to 0.5 by adding <math>\leq 2</math> mL of concentrated sulphuric acid.</p>  |
|  <p><b>4.</b> Cap, mix and then check the pH with narrow range pH paper.</p>                       |  <p><b>5.</b> Add approx. 18 g of muffed sodium sulphate and immediately shake until almost all is dissolved.</p>                                                   |  <p><b>6.</b> Add exactly 4.0 mL MTBE with IS.</p>                                                                            |
|  <p><b>7.</b> Shake vigorously for three minutes by hand.</p>                                      |  <p><b>8.</b> Allow the phases to separate for approximately 5 minutes.</p>                                                                                         |  <p><b>9.</b> Using a Pasteur pipet, transfer 3 mL of the upper MTBE layer to a 15 mL graduated conical centrifuge tube.</p> |

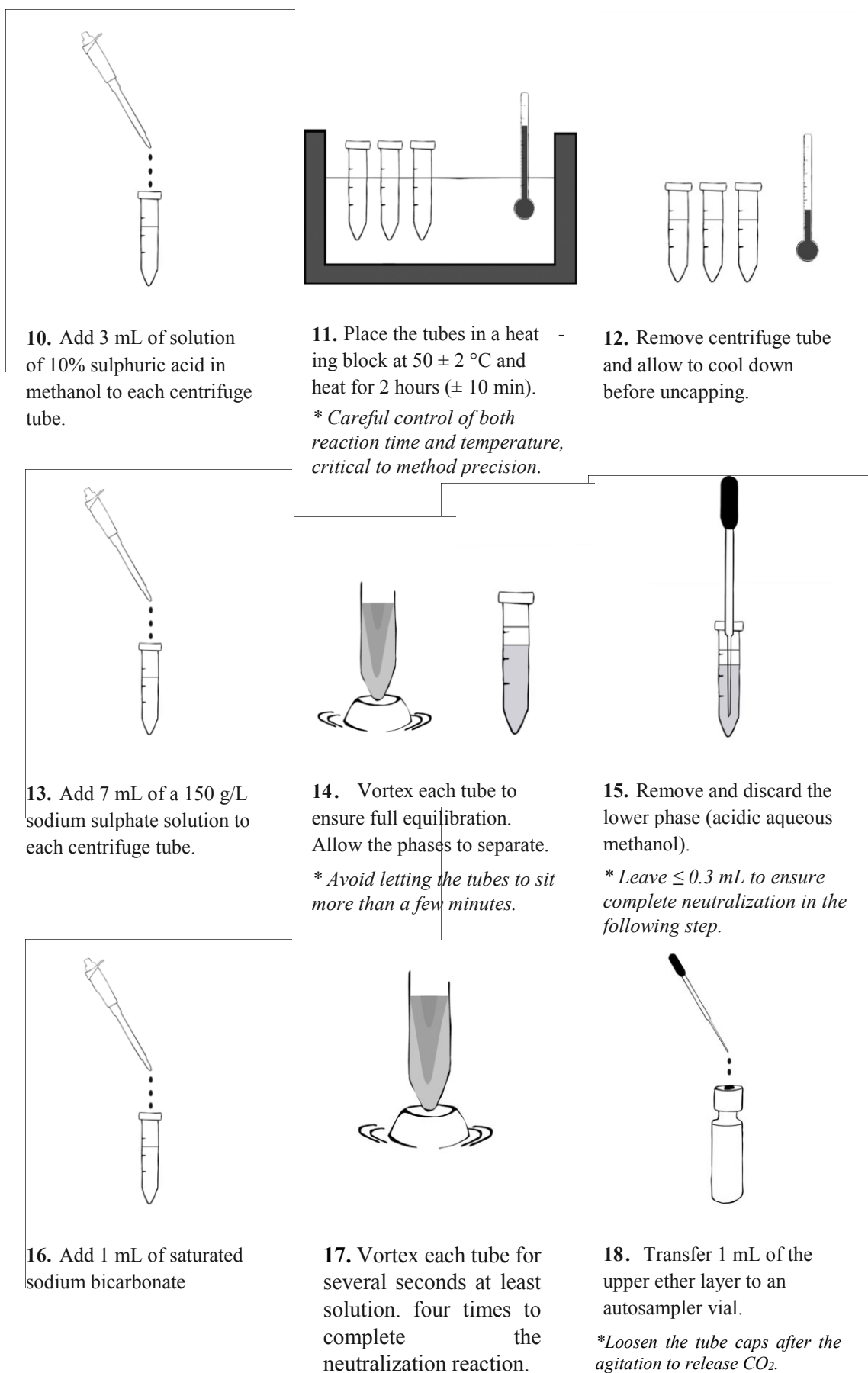


**Figure 4.2:** Illustrated methodology of HAAs extraction (*extraction method EPA 551.1*).

The extracted samples that were not introduced straight away to the chromatograph were stored in the freezer (-18°C) for a period that would not exceed 21 days, as the method suggests. Those that were not analysed within this period were discarded and are exempt from the results.

#### 4.5.2 Chromatographic analyses

The extracted samples were then analysed by gas chromatography so that the concentrations of the DBPs selected was quantified. The basic principle of GC analysis is based on the extracted sample volatilisation in the heated injector port, the separation of the target analytes into a specific column and their transportation by a carrier gas, and the ultimate detection of each component by a detector. More specifically, the chromatographic instrumentation is comprised of six components;

- i. Injector: Is the heated receiving port of the extracted samples, adjusted to a specific temperature to meet the volatilisation characteristics of the organic solution in which the target analytes are diluted. An injection port liner is used to make the connection between sample induction and the column, in addition of trapping non-volatile material to enter the GC system.
- ii. Carrier gas: The means by which the analytes are transported into the analytical column. The appropriate carrier gas should present inert nature, inability to be adsorbed by the static phase of the column, and high purity, to protect capillary columns. The supply and pressure controllers (*pneumatics*) must provide a stable and continuous carrier gas flow throughout the analysis.
- iii. Column: The selection of the chromatography columns is based on their ability to separate the various analytes before these reach the detector and therefore vary between different analysis. The basic principle of separating the components of a mixture is based on adsorption or distribution of these between two incompatible phases; *mobile* (carrier gas) and *stationary* (column filler).
- iv. Oven: Is a temperature gradient system in which the analytic column is located, responsible to regulate and increase the temperatures to meet the boiling points of the analytes carried in the column and facilitate their elucidation towards the detector.
- v. Detector: The purpose of a detector is to provide a response that is proportional to the concentration of a component that passes through and that this response is in the form of a measurable signal. It is selected based on the sensitivity, linearity and selectivity towards the target compounds.
- vi. Makeup gas: Is a high purity gas that is responsible to flow constantly through the detector to protect the sensitivity and ensure that all impurities are transported out of the system.

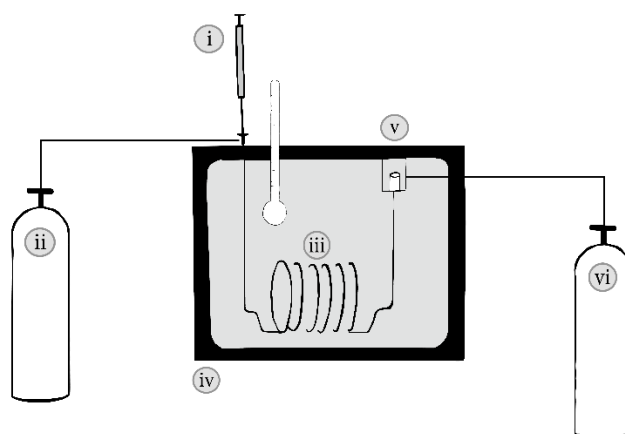


**Figure 4.3:** Simplified figure of chromatographic instrumentation i) injector, ii) carrier gas, iii) column, iv) oven, v) detector, vi) makeup gas.

#### 4.5.2.1 Chromatographic analyses of THMs and N-DBPs

The analysis of THMs and N-DBPs was performed in a PerkinElmer®Claruss®500 gas chromatograph located in the Roger Perry Laboratory (Department of Civil and Environmental Engineering) at Imperial College until October 2016. Due to laboratory issues, the completion of the THMs, HANs and HAcAm quantification was continued in Brunel University with the implementation of the same GC-ECD instrument and capillary column. These sets of data include the results from Round 4 of chloraminated systems C and D and the detailed phase of amide precursors study. This chromatograph was equipped with automated syringe injection and was coupled with an electron capture detector (ECD) that has proven to present high sensitivity and excellent selectivity for halogenated compounds. The primary column selected was a fused silica capillary column Rxi-5 Sil MS (Thames Restek UK), because the type of filling would provide adequate inertness of the target compounds in addition of having a high temperature tolerance and thus minimal bleed, needed for the high temperature analysis of the haloacetamides. The dimensions of the column were 30 m·0.25mm ID and film thickness of 0.25  $\mu\text{m}$ . In each analysis, 1  $\mu\text{L}$  of extract was injected by split less injection into the injector set at 170°C. This program needed to be modified from USEPA method to take into consideration the fact that all the THMs and HANs eluted from the capillary GC column between 35 and 145°C, however the HAcAms were not eluted until the oven temperature was at least 225°C. Therefore, an oven temperature program needed to be tailored to allow the proper resolution of all targeted DBPs (**Table 4.10**). So, the GC oven program initialized from 35°C and held for 22 minutes. Then, the temperature gradually increased with a rate of 10°C/min until reaching 145°C/min and then was held in this temperature for 2 minutes. Next, the temperature continued to increase up to 225°C/min by a rate of

20°C/min, which was maintained for 4 minutes. Finally, the temperature was further increased by a rate of 10°C/min yielding a final temperature of 260°C/min, which was held for 30 minutes. Thus, meaning that each sample had a total run time of 90 minutes.

**Table 4.10:** Gas chromatography specifications and operational conditions in modified EPA Method 551.1.

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|                        |                                                                                                                                                                                                                                                                                                                  |
|------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Primary Column:</b> | RXi 5Sil MS, 30m · 0.25mm ID, 0.25 µm film thickness                                                                                                                                                                                                                                                             |
| <b>Injector:</b>       | Injector temperature –170 °C; 2 mm straight quartz liner; injection volume 1 µL; splitless injection hold for 45 seconds then purge at 30 mL/min.                                                                                                                                                                |
| <b>Carrier Gas:</b>    | Helium ( <i>set at constant pressure</i> ), velocity 33 cm/sec.                                                                                                                                                                                                                                                  |
| <b>GC program:</b>     | <ul style="list-style-type: none"> <li>▪ HOLD at 35°C for 22 minutes.</li> <li>▪ INCREASE to 145°C at 10°C/min and hold at 145°C for 2 minutes.</li> <li>▪ INCREASE to 225°C at 20°C/min and hold at 225°C for 15 minutes.</li> <li>▪ INCREASE to 260°C at 10°C/min and hold at 260°C for 30 minutes.</li> </ul> |
| <b>Total time:</b>     | 90 min/ sample                                                                                                                                                                                                                                                                                                   |
| <b>Detector:</b>       | Agilent Micro ECD (150 µL); Detector temperature: 290 °C; Make up gas: 99.9% nitrogen at 30 mL/min.                                                                                                                                                                                                              |

---

Even though the experimental design included twenty DBPs to be analysed in this method, the final quantified DBPs were four THMs, five HANs and eight HAcAms. Monochloroacetonitrile (CAN), dibromochloroacetonitrile (DBCAN) and monochloroacetamide (CAcAm) were never detected above their detection limits in the actual samples nor in the stock standard solutions of the DBPs. The list of the quantified DBPs following this method together with the retention times in which their peaks were identified is summarised in **Table 4.11**.

**Table 4.11:** THMs, HANs and HAcAms quantified and their relative retention times during the analysis

| Peak # | Analyte                           | Retention time [minutes] | CAS No.     |
|--------|-----------------------------------|--------------------------|-------------|
| 1      | Chloroform                        | 3.84                     | 67-66-3     |
| 2      | Trichloroacetonitrile (TCAN)      | 4.66                     | 545-06-2    |
| 3      | Bromodichloromethane              | 5.67                     | 75-27-4     |
| 4      | Dichloroacetonitrile (DCAN)       | 6.34                     | 3018-12-0   |
| 5      | Monobromoacetonitrile (BAN)       | 8.10                     | 590-17-0    |
| 6      | Dibromochloromethane              | 11.43                    | 124-48-1    |
| 7      | Bromochloroacetonitrile (BCAN)    | 12.45                    | 83463-62-1  |
| 8      | Bromoform                         | 20.00                    | 75-25-2     |
| 9      | 1-Bromo-4-fluorobenzene (IS)      | 24.70                    |             |
| 10     | Dibromoacetonitrile (DBAN)        | 24.90                    | 3252-43-5   |
| 11     | Dichloroacetamide (DCAcAm)        | 29.40                    | 683-72-7    |
| 12     | Monobromoacetamide (BAcAm)        | 31.30                    | 683-57-8    |
| 13     | Trichloroacetamide (TCAcAm)       | 31.80                    | 594-65-0    |
| 14     | Bromochloroacetamide (BCAcAm)     | 32.78                    | 62872-34-8  |
| 15     | Bromodichloroacetamide (BDCAcAm)  | 33.46                    | 98137-00-9  |
| 16     | Dibromoacetamide (DBAcAm)         | 34.30                    | 598-70-9    |
| 17     | Dibromochloroacetamide (DBCAcAm)  | 35.25                    | 855878-13-6 |
| 18     | Tribromoacetamide (TBAcAm)        | 36.80                    | 594-47-8    |
| 19     | Monochloroacetonitrile (CAN)      | nd                       | 107-14-2    |
| 20     | Dibromochloroacetonitrile (DBCAN) | nd                       | 144772-39-4 |
| 21     | Monochloroacetamide (CAcAm)       | nd                       | 79-07-2     |

Yu and Reckhow (2017) recently argued that the HAcAms (DCAcAm, BAcAm and DBAcAm) identified to date using the most commonly employed analytical techniques are in fact levels of N-Cl-HAcAms. More specifically, their kinetic experiments indicated that HAcAms generated from chlorination are unstable and thus undergo instant N-chlorination. The result is a hydrogen bond between the amino hydrogen and hypochlorite oxygen that leads to the formation of equal amount of N-Cl-HAcAms, highly stable in water, detected at the same retention time. In this study though, the use of quenching agents (ammonium chloride and ascorbic acid) are proven to rapidly reduce the nitrogen-bound chlorine, converting the formed N-Cl-HAcAms back to simple HAcAms. This hypothesis validates our findings and showed that the HAcAms identified are not N-Cl-HAcAms but simple HAcAms. However, this finding raises concerns for water consumer's risk, as they might be exposed to a family of compounds even more toxicological potent than HAcAms and HANs, since disinfectant residuals are not quenched in real distribution systems.

#### 4.5.2.2 Chromatographic analysis of HAAs

The analysis of the nine brominated and chloraminated haloacetic acids (HAAs) was performed in a PerkinElmer®Clarus®500 gas chromatograph located in Environmental Chemistry Laboratory (Institute of Environment, Health and Societies) at Brunel University London. The instrument was equipped with automated syringe injection and was coupled with an electron capture detector (ECD), known to be the most appropriate detector for compounds containing at least one halogen atom.

The primary column selected was a fused silica capillary column with chemically bonded (14% cyanopropylphenyl, 86% dimethylpolysilo) DB-1701 (Agilent Technologies), of low/mid-polarity that enables analysis temperatures up to 300°C. The dimensions of the column were 30 m·0.25mm ID and film thickness of 0.25 µm. In each analysis, 1 µL of extract was injected by splitless injection into the injector set at 210°C. The GC oven program initialized from 40°C and held for 10 minutes. Then, the temperature gradually increased with a rate of 2.5°C/min until reaching 65°C/min. Next, the temperature continued to increase up to 85°C/min by a rate of 10°C/min, and finally, the temperature was further increased by a rate of 20°C/min yielding a final temperature of 205°C/min, which was held for 7 minutes. Thus, meaning that each sample had a total run time of 35 minutes.

The list of the quantified HAAs following this method together with the retention times in which their peaks were identified is summarised below in **Table 4.13**.

**Table 4.12:** Gas chromatography specifications and operational conditions in modified EPA Method 552.3.

|                        |                                                                                                                                                                                                                                                |
|------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Primary column:</b> | DB-1701, 30m · 0.25mm ID, 0.25 µm film thickness.                                                                                                                                                                                              |
| <b>Injector:</b>       | Injector temperature – 210°C; 2 mm straight quartz liner; injection volume 1 µL;<br>splitless injection hold for 45 seconds then purge at 30 mL/min.                                                                                           |
| <b>Carrier Gas:</b>    | Helium (set at constant pressure), velocity 33 cm/sec.                                                                                                                                                                                         |
| <b>GC program:</b>     | <ul style="list-style-type: none"> <li>▪ HOLD at 40°C for 10 minutes.</li> <li>▪ INCREASE to 65°C at 2.5°C/min.</li> <li>▪ INCREASE to 85°C at 10°C/min.</li> <li>▪ INCREASE to 205°C at 20°C/min, and hold at 205°C for 7 minutes.</li> </ul> |
| <b>Total time:</b>     | 35 min/ sample                                                                                                                                                                                                                                 |
| <b>Detector:</b>       | Agilent Micro ECD (150 µL); detector temperature: 290 °C; Make up gas:<br>99.9% nitrogen at 20 mL/min.                                                                                                                                         |

**Table 4.13:** HAAs quantified and their relative retention times during the analysis.

| Peak # | Analyte                          | Retention time [minutes] | CAS No.    |
|--------|----------------------------------|--------------------------|------------|
| 1      | Monochloroacetic acid (MCAA)     | 8.10                     | 79-11-8    |
| 2      | Monobromoacetic acid (MBAA)      | 13.86                    | 79-08-3    |
| 3      | Dichloroacetic acid (DCAA)       | 15.50                    | 79-43-6    |
| 4      | Trichloroacetic acid (TCAA)      | 17.71                    | 76-03-9    |
| 5      | 1,2,3 Trichloropropanone (IS)    | 21.00                    |            |
| 6      | Bromochloroacetic acid (BCAA)    | 21.60                    | 5589-96-8  |
| 7      | Bromodichloroacetic acid (BDCAA) | 23.60                    | 71133-14-7 |
| 8      | Dibromoacetic acid (DBAA)        | 24.00                    | 631-64-1   |
| 9      | Dibromochloroacetic acid (DBCAA) | 25.50                    | 5278-95-5  |
| 10     | Tribromoacetic acid (TBAA)       | 26.78                    | 75-96-7    |

### 4.5.3 Data analysis & Quality Control

The measurements of any analytical chromatographic technique are recorded as signals and require the calibration of chromatographs with standard solutions containing known concentrations of the target compounds. Therefore, during each analysis calibration standards for THMs, HAAs, HANs and HAcAms were prepared from the stock standard solutions by spiking calibration samples of at least six different concentrations. These calibration standards were treated, extracted and analysed the same way as the actual water samples dedicated in identifying these organic compounds. The concentrations selected to facilitate calibrations were distributed in the range in which the target compounds were expected to be identified in the actual samples in order to achieve more representative and accurate equations (*Table 4.14*). The target compounds were available as concentrated liquid standard mixes, as individual liquid analytes and as solid substances. However, to facilitate calibration spiking all stock solutions were prepared separately or in combination in a concentration of 1200 µg/L. In addition to the calibration standards, two blank samples were also extracted and analysed to ensure that there are zero interferences from laboratory glassware or reagents and proactively eliminate sample processing troubleshooting. Following the chromatographic analysis of each calibration sample, a calibration curve was created by the graphical representation of the numerical values identified (area of peak areas), normalized by the relative numerical value of the internal standard in each sample. The equation generated from each regression analysis was used to quantify further the unknown concentration of each target compound in the actual water samples. A typical example of calibration curves used in one of the analysis, together with the regression equations and the  $R^2$  are demonstrated in **Figure 4.4**.

Another important quality control parameter is the determination of method detection levels for each target compound (MDL) during the methods selected for the current study. MDL is the threshold concentration of an analyte that can be accurately quantified with a certain method in an unknown water sample and it is determined by the fortification, extraction and analysis of *seven* replicate samples spiked with the same concentration. The spiked concentration to determine the method detection limits is estimated to be 2 to five times the background levels or approximately 100 times lower than the maximum concentration used for calibration.

The calculation of the MDL is based on the following equation:

$$MDL = S \cdot t_{(n-1, 1-\alpha=0.99)} = \sigma \cdot 3.143 \quad \text{Equation 4.2}$$

where,

- $t_{(n-1, 1-\alpha=0.99)}$ : Students t value for the 99% confidence level with n-1 degrees of freedom  
(for 7 replicates equals 3.143).  
n: Number of replicates.  
S: Standard deviation of the replicate analyses.

Furthermore, another essential parameter for the validation of the method selected is the recovery rate of each target compound, expressed in percentages. This measurement demonstrates the capacity level of a given method or instrument to identify each compound. This was achieved by spiking duplicate RO water samples with 2 different known concentrations (25% and 75% of calibration range) of the target DBP stock solutions to investigate the amount of these concentrations determined from the extraction method and instrument sensitivity. The DBPs quantified in this study together with their calibration concentrations, method detection limits and recovery rates can be found in *Table 4.14*.

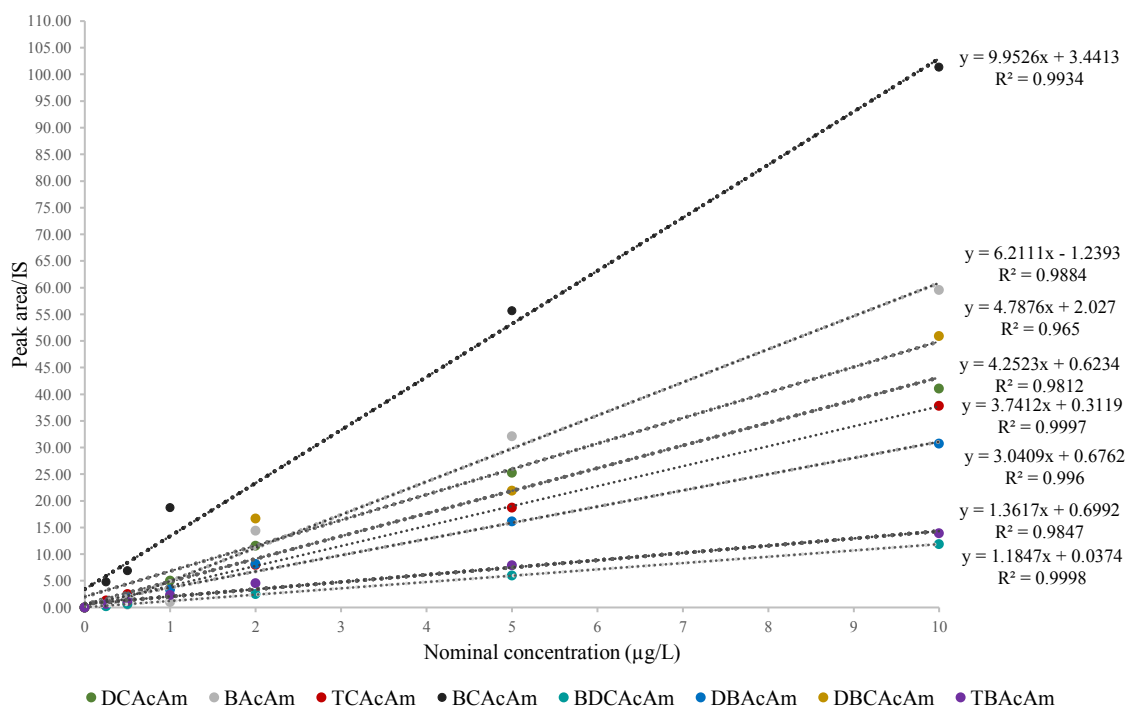


**Figure 4.4:** Typical calibration curve for HAcAms together with the equations and R<sup>2</sup> values.

**Table 4.14:** Concentration ranges, MDL and recovery rates of THMs, HAAs, HANs and HAcAms.

| Target Analytes          | Calibration concentration range               | MDL<br>[µg/L] | Recovery rate<br>[%] |
|--------------------------|-----------------------------------------------|---------------|----------------------|
| <b>Trihalomethanes</b>   | <i>0, 1.0, 2.0, 5.0, 10.0, 25.0 µg/L</i>      |               |                      |
|                          | CHCl <sub>3</sub> Chloroform                  | 0.4           | 108                  |
|                          | CHBrCl <sub>2</sub> Bromodichloromethane      | 0.3           | 110                  |
|                          | CHBr <sub>2</sub> Cl Dibromochloromethane     | 0.2           | 110                  |
|                          | CHBr <sub>3</sub> Bromoform                   | 0.4           | 98                   |
| <b>Haloacetic acids</b>  | <i>0, 1.0, 2.0, 5.0, 10.0, 25.0 µg/L</i>      |               |                      |
|                          | MCAA Monochloroacetic acid                    | 0.2           | 95.8                 |
|                          | MBAA Monobromoacetic acid                     | 0.5           | 92.2                 |
|                          | DCAA Dichloroacetic acid                      | 0.2           | 93.8                 |
|                          | TCAA Trichloroacetic acid                     | 0.2           | 105                  |
|                          | DBAA Dibromoacetic acid                       | 0.1           | 98                   |
|                          | BCAA Bromochloroacetic acid                   | 0.1           | 101                  |
|                          | BDCAA Bromodichloroacetic acid                | 0.7           | 110                  |
|                          | DBCAA Dibromochloroacetic acid                | 1.0           | 108                  |
|                          | TBAA Tribromoacetic acid                      | 1.0           | 90.6                 |
| <b>Haloacetonitriles</b> | <i>0, 0.25, 0.5, 1.0, 2.0, 5.0, 10.0 µg/L</i> |               |                      |
|                          | MCAN Monochloroacetonitrile                   | n/a           | n/a                  |
|                          | MBAN Monobromoacetonitrile                    | 0.1           | 90                   |
|                          | DCAN Dichloroacetonitrile                     | 0.1           | 90                   |
|                          | TCAN Trichloroacetonitrile                    | 0.1           | 95                   |
|                          | DBAN Dibromoacetonitrile                      | 0.2           | 95                   |
|                          | BCAN Bromochloroacetonitrile                  | 0.2           | 110                  |
|                          | BDCAN Bromodichloroacetonitrile               | n/a           | n/a                  |
|                          | DBCAN Dibromochloroacetonitrile               | 0.5           | 80                   |
|                          | TBAN Tribromoacetonitrile                     | n/a           | n/a                  |
| <b>Haloacetamides</b>    | <i>0, 0.25, 0.5, 1.0, 2.0, 5.0, 10.0 µg/L</i> |               |                      |
|                          | MCAcAm Monochloroacetamide                    | n/a           | n/a                  |
|                          | MBAcAm Monobromoacetamide                     | 0.1           | 70                   |
|                          | DCAcAm Dichloroacetamide                      | 0.1           | 85                   |
|                          | TCAcAm Trichloroacetamide                     | 0.1           | 80                   |
|                          | DBAcAm Dibromoacetamide                       | 0.1           | 88                   |
|                          | BCAcAm Bromochloroacetamide                   | 0.1           | 73                   |
|                          | BDCAcAm Bromodichloroacetamide                | 0.1           | 70                   |
|                          | DBCAcAm Dibromochloroacetamide                | 0.1           | 71                   |
|                          | TBAcAm Tribromoacetamide                      | 0.1           | 70                   |

All experiments were performed in duplicates to enable t-test comparisons with a 95% confidence interval. Experiments were triplicated, whenever possible, in cases when duplicates differed significantly. The implementation of a quality control plan throughout the whole analysis, with calibration curves, method detection limits, analytes recovery rates and blanks demonstrated the precision and reproducibility of the databases created.

## 4.6 Bromine incorporation factor

The bromine incorporation factor (BIF) is characterised as the ratio of the molar concentration of incorporated bromide into a given class of DBPs divided by the total molar concentration of chlorine and bromine in that class (Hua and Reckhow 2012). The degree by which bromine is incorporated in the DBPs identified is a useful indicator to compare the degree of bromination of different DBP classes in the presence of chlorine or chloramine, and therefore prioritise minimisation strategies. Brominated DBP species may be more genotoxic and carcinogenic than the chlorinated analogues (Richardson et al. 2007). In addition, understanding the bromide incorporation patterns into DBPs may be also used to assess the interconnection between the different DBP classes and if correlations exist could be used as a prediction tool for the brominated compounds that are difficult to be identified through analytical techniques.

The bromide incorporation factor (BIF) was calculated based on the following Equations (4.3-4.8), where concentrations are on a molar basis:

$$BIF (THMs) = \frac{[CHBrCl_2] + 2 \cdot [CHBr_2Cl] + 3 \cdot [CHBr_3]}{[CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]} \quad \text{Equation 4.3}$$

$$BIF (di-HAAs) = \frac{[BCAA] + 2 \cdot [DBAA]}{[DCAA] + [BCAA] + [DBAA]} \quad \text{Equation 4.4}$$

$$BIF (tri-HAAs) = \frac{[BDCAA] + 2 \cdot [DBCAs] + 3 \cdot [TBAA]}{[TCAA] + [BDCAA] + [DBCAs] + [TBAA]} \quad \text{Equation 4.5}$$

$$BIF (di-HANs) = \frac{[BCAN] + 2 \cdot [DBAN]}{[DCAN] + [BCAN] + [DBAN]} \quad \text{Equation 4.6}$$

$$BIF (di-HAcAms) = \frac{[BCAcAm] + 2 \cdot [DBAcAm]}{[DCAcAm] + [BCAcAm] + [DBAcAm]} \quad \text{Equation 4.7}$$

$$BIF (tri-HAcAms) = \frac{[BDCAcAm] + 2 \cdot [DBCAcAm] + 3 \cdot [TBAcAm]}{[TCAcAm] + [BDCAcAm] + [DBCAcAm] + [TBAcAm]} \quad \text{Equation 4.8}$$

In order to achieve a better comparison, the results of the above calculations were normalised by the number of halogens; dihalogenated and trihalogenated compounds were divided by two and three, respectively. This normalisation will produce BIF values between 0 (all chlorinated species) and 1 (all brominated).

## 4.7 Statistical analyses & correlations

Statistical analysis and correlations were performed in Excel and a statistics software SPSS (IBM). Due to limitations of the analytical procedures or the low occurrence of DBP species, several measurements were identified as below the method detection limits (MDL). In this study, all results that were below the method detection limits (MDL) were excluded from mean concentration calculations of individual compounds and total DBP class concentrations, and from other statistical analyses. A detailed table that summarises the DBP survey in numbers and the frequency that each DBP species was identified in the analysis can be found in **Appendix A: Table A.4**.

The calculation of median values, instead of mean values, was selected to analyse the DBPs results and design the graphs in Chapter 5, to achieve homogenous and representative results analysis, by eliminating the effect of potential individual outliers in the database.

To investigate any correlations between the water quality parameters and the DBP levels in the real water samples collected in this study, Pearson product moment correlation coefficient ( $r$ ) was calculated in all chlorinated and chloraminated systems, separately, by using the raw data in the analysis.

## Chapter 5. Results

Trihalomethanes (THM), haloacetic acids (HAA), haloacetonitriles (HAN) and haloacetamides (HAcAm) and a variety of water quality parameters were monitored in four full-scale distribution systems during four seasonal sampling rounds and via the implementation of simulated distribution system tests. The water quality parameters analysed included chlorine residual, TOC concentration, pH, temperature, bromide and UV absorbance, and are summarised in **Table 5.1** for all four selected WTW. This chapter examines the changes in DBP concentration, DBP speciation and water quality with increasing water age, including the effects of seasons in two systems receiving free chlorine as the final disinfectant, and two systems receiving chloramines as the final disinfectant. This was the first time simulated distribution system (SDS) tests were validated to accurately predict the formation and speciation of haloacetamides (HAcAms) and haloacetonitriles (HANs) in distribution systems (Sfynia et al., 2017). In addition, this is the most complete and consistent database of regulated and unregulated DBPs in England and one of the few such existing databases in the world currently. Moreover, this chapter includes a comparative disinfectant analysis of the selected systems as a means of DBP minimisation, since for the systems currently chlorinated, SDS tests were also performed with the use of chloramines in the same treated water and the opposite. The results obtained during chlorination were compared with those obtained during the implementation of SDS tests with the use of chloramines.

Correlations (linear) were calculated between DBP concentrations and water age or selected water quality parameters, to identify one or more parameters that could be used as surrogate(s) of the DBPs investigated. When selecting the sampling locations of each treatment works, consideration was given to select locations with similar water age with those selected for the SDS tests. In this chapter, illustrative graphs and summarising tables are presented. The complete database of DBP occurrence and speciation quantified in this study is presented in **Appendix B** - Database of actual and SDS tests in WTW A, B, C, D (4 Rounds).

The discussion that follows is organised by type of disinfectant residual used in the water treatment works studied. The results discussed below have been interpreted in consideration of the limitations of the analytical methods in terms of MDL of each species, standard deviation between the samples, analytes recovery rates, method performance and analysis blanks.

**Table 5.1:** Summary of water quality characteristics of the selected chlorinated and chloraminated WTW during the seasonal samplings.

| WTW               | Units                | A            |           |         |          | B            |           |           |          | C              |         |         |           | D              |         |         |         |
|-------------------|----------------------|--------------|-----------|---------|----------|--------------|-----------|-----------|----------|----------------|---------|---------|-----------|----------------|---------|---------|---------|
| Sampling rounds   |                      | 1            | 2         | 3       | 4        | 1            | 2         | 3         | 4        | 1              | 2       | 3       | 4         | 1              | 2       | 3       | 4       |
| Date              |                      | Sept 15'     | Feb 16'   | May 16' | Sept 15' | Sept 15'     | Feb 16'   | May 16'   | Sept 15' | Oct 15'        | Mar 16' | Jun 16' | Sep 16'   | Oct 15'        | Mar 16' | Jun 16' | Sep 16' |
| Disinfectant type | -                    | Chlorination |           |         |          | Chlorination |           |           |          | Chloramination |         |         |           | Chloramination |         |         |         |
| Disinf. residual  | mg/L Cl <sub>2</sub> | 0.9-0.2      | 0.7-0.2   | 1.0-0.2 | n/a      | 0.6-0.2      | 0.6-0.3   | 0.6-0.4   | 1.1-0.4  | 1.2-0.9        | 1.0-0.3 | 0.9-0.5 | 1.0-0.5   | 0.6-0.2        | 0.8-0.6 | 1.0-0.2 | 1.0-0.2 |
| Water temperature | °C                   | 17.0         | 8.0       | 14.0    | 20.0     | 17.0         | 8.0       | 14.0      | 20.0     | 14.0           | 8.0     | 17.0    | 20.0      | 14.0           | 8.0     | 17.0    | 20.0    |
| TOC               | mg/L C               | 3.1          | 3.4-3.7   | 3.3-3.6 | 3.1-3.4  | 3.8          | 3.3-3.6   | 4.0-4.2   | 3.5-3.7  | 3.1-3.3        | 3.3-3.5 | 3.1-3.2 | 2.2-2.6   | 2.8-3.3        | 2.8     | 1.8     | 2.7-2.8 |
| pH                | -                    | n/a          | 7.4-7.6   | 7.4-7.5 | 7.0-7.1  | n/a          | 7.4-7.6   | 7.0-7.5   | 7.2      | 7.2-7.4        | 7.6     | 7.1-7.4 | 7.4-7.5   | 6.5-7.3        | 7.4-7.6 | 7.3-7.4 | 7.5     |
| Bromide           | µg/L                 | <12.0        | <12.0     | <12.0   | <12.0    | <12.0        | 18.3      | <12.0     | 12.0     | 82             | 85.1    | 76      | 80.0      | 13.2           | 19.9    | 26.4    | <12.0   |
| UV <sub>abs</sub> | l/M·cm               | n/a          | 0.04-0.06 | 0.06    | n/a      | n/a          | 0.04-0.06 | 0.04-0.07 | n/a      | n/a            | 0.06    | 0.04    | 0.05-0.06 | 0.03-0.05      | 0.06    | 0.04    | 0.05    |
| SUVA              | -                    | n/a          | 1.2-1.6   | 1.8     | n/a      | n/a          | 1.2-1.9   | 1.1-1.6   | n/a      | n/a            | 1.7     | 1.4     | 2.3-2.6   | 1.0-1.7        | 2.1-2.3 | 2.2-2.3 | 1.9     |

## 5.1 Occurrence of regulated and unregulated DBPs in actual distribution systems

### 5.1.1 In chlorinated water supply systems

Two of the distribution systems studied used free chlorine as the final disinfectant, and are designated as A and B. *Table 5.2* and *Table 5.3* present the results of THMs, HAAs, HANs and HAcAms total concentrations obtained in the selected downstream locations (L1, L2, L3), of treatment works A and B, respectively, during all seasonal sampling rounds together with the TOC and bromide measurement of the final water in each treatment work. A more detailed database on the water quality parameters can be found in Appendix A.7, whereas the complete database from the annual distribution monitoring in Appendix B.

#### 5.1.1.1 Trihalomethanes (THMs) in chlorinated systems

Total trihalomethanes concentrations increased with the increase of water age, whilst chlorine residual decreased. This trend was observed during all sampling rounds at both chlorinated water works A and B, and is consistent with previous published work and the company's historical data. In **WTW A**, the lowest concentrations observed were at the water works reservoir (A-L1), where water age was estimated to be between 6-12 hours, whereas the highest concentrations at the water reservoir in distribution (A-L3), estimated to be characterised with water ages between 72-106 hours. The increases in THMs concentration from the first and the last downstream location were significant and consistent, since the concentration in A-L1 was doubled (*average increase*: 49.4%) in the majority of the sampling rounds by the time the water would reach A-L3. Also, it was important because the distribution system of WTW A presented areas with even longer water ages of > 144 hours that were excluded from the sampling, and possibly presented even higher THM increases in reality. In **WTW B**, THM concentrations also increased with water age, though some variations were observed in the increases in percentages ranging from 44 to 50.8%, between the seasonal rounds. This was possibly due to the ambiguity of the exact water ages in the distribution system and possibility of WTW B being sampled in lower water ages than WTW A. The sampling of real water samples, characterised by limited pH variations (pH range 7-7.7) did not enable any correlation between the mediated effect of this parameter in the formation of THMs and other DBP classes.

The results from the actual distribution networks indicated that THMs concentrations were significantly higher in both distribution systems, particularly in the downstream locations characterised by high water ages. Water utilities in England typically have internal limits for total THM concentration set at 50 µg/L, individual concentrations measured in the highest water age location (A-L3) exceeded this limit during all samplings in the system of water work A, with concentrations ranging from 52.9 (winter) to 71.0 µg/L

(summer). It is noteworthy, that during the summer sampling round this limit was slightly exceeded even in the medium water age location (A-L2) with concentration of 51.9 µg/L. In water works B, a similar trend was observed but the internal limit in the location with the highest water age (B-L3) was exceeded only in three of the four sampling rounds (autumn, spring and summer), whereas this was not exceeded in any intermediate location. **Figure 5.1** shows the speciation of THM results obtained from the selected distribution location of both WTW A and B. The results show that the brominated species (e.g. dibromochloromethane, bromoform) represented most of the total THM concentrations in these systems, because of the bromide concentrations present in the final water of these systems, with the most abundant trihalomethane being dibromochloromethane. The weight fraction of chlorine-containing THM (*chloroform*) decreased with increasing water age in WTW B (*average of 31.9% decrease*) during all sampling rounds, especially until B-L2, or remained in similar levels, mainly until B-L3. As expected, these decreases were associated with minimal increases in the concentrations of the bromine-containing THMs. Nevertheless, the opposite was observed in WTW A, where the weight fraction of chloroform in THMs was slightly increasing (*average of 25.5%*) from A-L1 to A-L3, with a subsequent slight decrease of the bromine-containing THMs. The latter pattern is not consistent with literature, as the bromine-containing DBPs are reported to form slower than the chlorinated ones. As such, the weight fraction for chloroform was expected to decrease with water age, as calculated for WTW B. This deviation may be related to the higher ratio of chlorine to bromine in the network of WTW A, due to the increased chlorine demand in this system.

#### 5.1.1.2 Haloacetic acids (HAAs) in chlorinated systems

The concentrations of haloacetic acids (HAAs) had a different behaviour in the distribution of chlorinated systems A and B in comparison with the THMs. Data obtained from **WTW A** showed a slight increase between L1 and L2, in approximately > 12 and 48 hours, but then a reduction is observed (7.4-22%), as water age increased and chlorine residual decreased. This was most likely due to HAA biodegradation at higher water ages, due to bacterial activity in the water or biofilm growth in the pipes (Bayless and Andrews 2008; Zhang et al. 2009). Nevertheless, it could also be due to chemical dehalogenation via water contact with the unlined cast iron pipes of the distribution network (Hozalski et al. 2001; Tang et al. 2013), typical material of the largest part of the selected networks. The pH values, which remain relatively stable in downstream locations, did not suggest any base catalysed hydrolysis that resulted in tri-HAAs reduction (Reckhow et al. 1990) regardless the increase of THMs. Literature argues that while mono- and di- HAAs

species are relatively susceptible to biodegradation, tri-HAAs are more recalcitrant to biological reduction (Zhou and Xie 2002) but more receptive to chemical dehalogenation than the other two groups (Hozalski et al. 2008; Tang et al. 2013; Wang et al. 2013). Thus, a way to understand the source of HAAs reduction would be by examining the behaviour of HAAs species in the distribution networks. In our case all HAAs species follow reductions at some point of the distribution systems, nevertheless the reduction of mono- and di-HAAs was significantly more pronounced than that of tri-HAAs in WTW A and B. This finding suggested that the HAAs degradation in the selected chlorinated distribution networks was most likely a combination of biological and chemical reactions, with the biodegradation being the most crucial HAAs reduction process. Even though during the three rounds that presented the highest water temperatures, HAAs reduction was observed at approximately >12 hours, during the 2<sup>nd</sup> round (*winter*) total concentration continued to slightly increase until the location with the highest water age. This is possibly due to the low water temperatures that delayed or postponed chemical reactions related to chlorine consumption or HAA degradation. Also, the rate by which HAAs were increased and decreased were fluctuating between the sampling rounds, with the highest degradation rate of 22% between A-L2 and A-L3 in the first round, resulting in HAA concentrations in the location with the highest water age to be even lower than those reported in the location with the lowest water age. The maximum HAA concentration was reported to be 66.9 µg/L in the medium water age location (A-L2) during the first round (*autumn*) and the minimum in the same location in the second round (*winter*). The biodegradation of HAAs was more pronounced when water temperature was high and the free chlorine was low (<0.5 mg/LCl<sub>2</sub>). This trend concerning HAAs degradation in distribution networks that are characterised by low disinfection residual and high bacterial activity, has been previously discussed by many other researchers (Koch et al. 1991; Rossman et al. 2001; Symanski et al. 2004; Baribeau et al. 2006). In **WTW B** (Table 5.3), unlike WTW A, HAAs started to degrade in lower water ages between >12 and 48 hours (*median rate of 5%*), and then were slightly increased until 72-106 hours (*median rate of 17%*), during Round 2 (*winter*) and Round 3 (*spring*). This is not necessarily linked to low chlorine residual reported during earlier stages, since WTW A presented even lower in similar water ages, but may be related to extended biological activity in the pipes during these periods. During Round 4 on the other hand HAA concentrations were following an increase rate until 48 hours (*of 14.9%*) and then started to degrade (*of 10.4%*), similarly to the HAAs pattern in WTW A. However, the degradation observed in B WTW was not as pronounced as in A WTW, resulting in HAAs in this system to be higher in the location with the high water ages in comparison with those in the location

of the lowest water ages. The higher chlorine residuals reported and the possibility of the downstream locations of WTW B being at the lowest point of the water age range are possible explanations for lower HAAs biodegradation. The maximum HAA concentration was reported to be 59.4 µg/L in the high water age location (B-L3) during the first round (*autumn*) and the minimum with 13.6 µg/L in the medium water age location (B-L2) during the second round (*winter*). The HAAs concentrations that were measured during the sampling of the downstream location of the two chlorinated water works, agreed with previous published report on HAAs in the UK (Parsons and Goslan 2009) where values in distribution ranged from 8-75 µg/L (*median*: 20.8 µg/L). Unfortunately, conclusions for HAAs are not able to be withdrawn from Round 1 of water work B, as sampling handling was not appropriate for analysis. Even though there is no internal limit for HAAs set by the water utilities that operate in England, if a marker concentration of 40 µg/L is considered, if the regulatory limit is set to half due to their similar occurrence with THMs, then this concentration would have been exceeded even in the first downstream location with the lowest water age (A-L1), during the months with the highest temperatures.

Concerning the HAA speciation, the dominant HAA species was dichloroacetic acid (DCAA), followed by dibromoacetic acid (DBAA) and bromodichloroacetic acid (BDCAA), that agreed with previous studies on HAAs in distribution with similar bromide levels (<12 -18.3 µg/L) (Baribeau et al. 2006; Graham et al. 2009). **Figure 5.2**, presents the total HAAs speciation as a function of the water age ranges identified in the chlorinated water works. It is noteworthy, that the concentrations of the dominant species are reported to be significantly elevated during the sampling rounds with the highest water temperatures, which means that HAAs speciation was dependent not only in the NOM characteristics but also on the water temperature. In general, the weight ratios of bromine containing HAAs species was always higher than that of the chlorinated ones and followed an increase between L1 and L2 and a reduction between L2 and L3, ranging from 46.5-78.6% and 45.6-74.2% in WTW A and WTW B, respectively. However, during Round 2 (*winter*), bromide containing HAAs were decreasing with water age constantly. This was possibly linked to the reduced reactivity of chlorine at lower temperature, which was prolonging the formation of chlorinated species in longer water ages. Also, the proportion of the total HAAs comprised by the five (HAA<sub>5</sub>) that are currently regulated ranged between 54.9-83.1% (*median* 67.3%) and 52.8-76.9% (*median* 67.9 %), for WTW A and B, respectively. These calculations showed, that in the chlorinated systems studied, the non-regulated HAAs represented a significant proportion of the total HAAs and is recommended to be included in DBPs monitoring surveys for accurate observations. Generally, the HAA<sub>5</sub>

to total HAAs weight ratios increased slightly or remained stable until the location of medium water age (L2) and then started to drop until the location with the highest water age (L3), in both distribution systems. The time step in which these decreases were reported were consistent with the reduction of HAA concentrations due to biodegradation, previously discussed. In fact, it is known from literature that mono- and di-haloacetic acids (RAAs and R<sub>2</sub>AAs), representative species of HAA<sub>5</sub>, are more prone to biodegradation than the tri-haloacetic acids (R<sub>3</sub>AAs), representative species of the non-regulated HAAs (Bayless and Andrews 2008).

Overall, a general observation would be that HAAs concentrations are not characterised by significant changes within the distribution system, as in some cases the initial concentration is very similar to the one observed after 72-106 hours, albeit the intermediate fluctuations (Koch et al. 1991; Singer et al. 2002; Baribeau et al. 2006). So, it can be said that HAAs behave differently than THMs which presented a consistent and significant increase with water age, already confirmed by other studies.

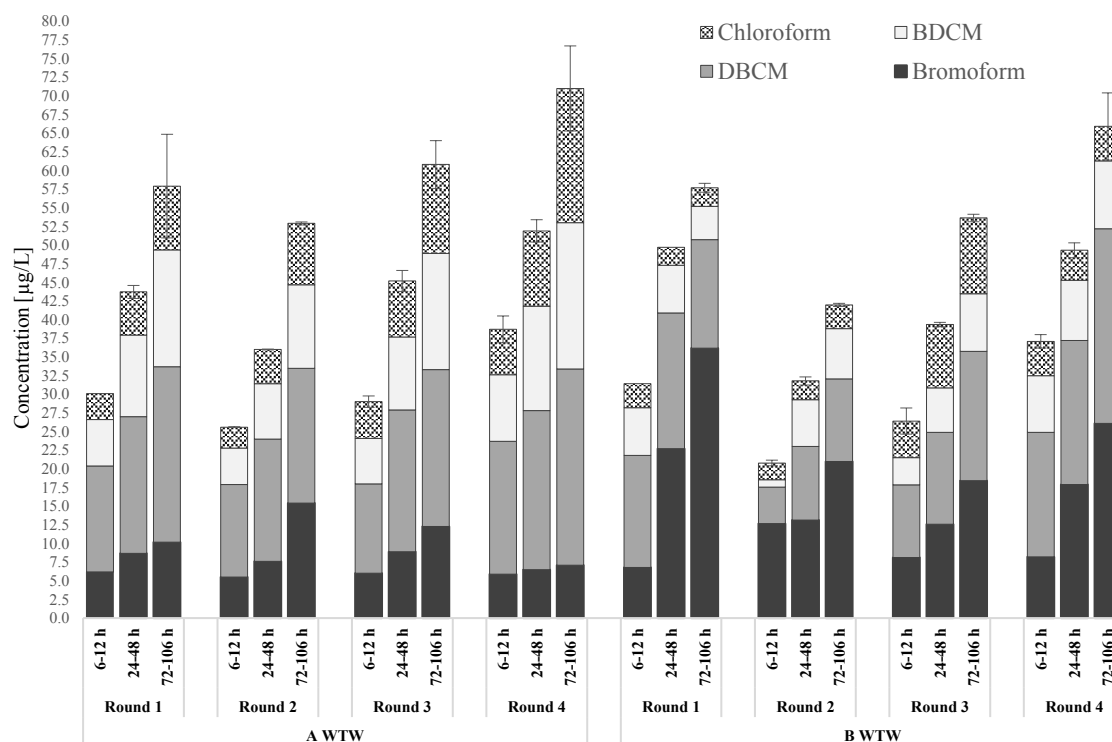


**Figure 5.1:** THM speciation as a function of water age measured in chlorinated systems A and B. (Round 1-Sept 15', Round 2-Feb 16', Round 3-May 16', Round 4-Aug 16').

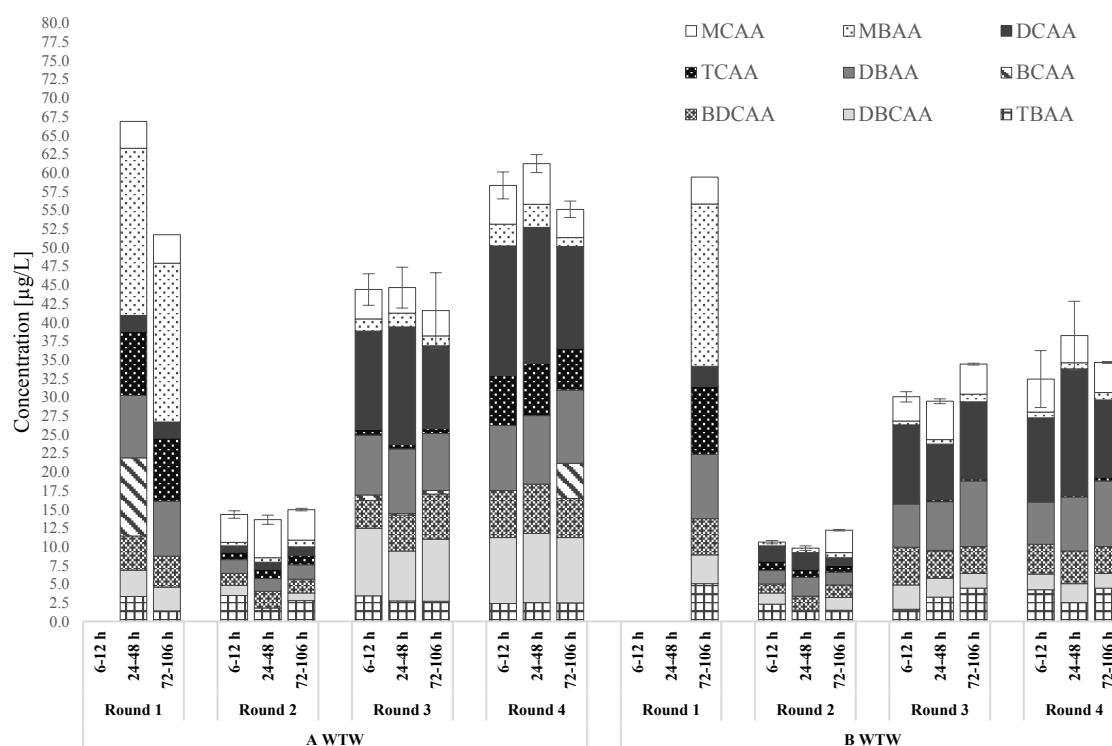


**Figure 5.2:** HAA speciation as a function of water age measured in chlorinated systems A and B. (Round 1-Sept 15', Round 2-Feb 16', Round 3-May 16', Round 4-Aug 16').

### 5.1.1.3 Haloacetonitriles (HANs) in chlorinated systems

The research also included the quantification of nitrogenous disinfection by-products, specifically haloacetonitriles (HANs) and haloacetamides (HAcAms), since information concerning their occurrence and behaviour in distribution systems was lacking.

In the chlorinated distribution systems sampled (A and B), comparable HANs and HAcAms concentrations were quantified during all sampling rounds in all downstream locations sampled. From the seven selected HANs, only five of them were able to be identified, whereas from the nine HAcAms, eight were able to be identified with the analytical methods applied. When these concentrations are compared against those of total THMs and HAAs, N-DBPs occurred in significantly lower amounts, and represented almost 10% THMs and 11.5% HAAs, which is confirmed with other studies (Oliver 1983; Krasner et al. 2006). In chlorinated systems, haloacetonitriles were found at the highest sum concentrations with 4.8 µg/L (*median*), followed by HAcAms with 4.0 µg/L (*median*). The N-DBP concentrations identified in this study largely agreed with the ranges detected from a previous nationwide occurrence survey in England (Templeton et al. 2012; Bond et al. 2015), in which HANs and HAcAms (3 *species*) reported with total mean concentrations of 3.2 µg/L and 1.5 µg/L, respectively. In addition, the N-DBP results were comparable with those identified in a previous US DBP survey by Krasner et al. (2006), where HANs (5 *species*) and HAcAms (5 *species*) were reported in levels of 3 µg/L and 1.5 µg/L, respectively.

More specifically, in the chlorinated distribution system of WTW A median HAN concentrations were reported to be 4.1 µg/L, 5.9 µg/L and 4.9 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. However, there is no consistent trend observed in relation with their behaviour with water age since their concentrations are very similar between the sampling locations and the sampling rounds. In two of the sampling rounds, those with the higher water temperatures reported (*Round 1-autumn & Round 4-summer*), the sum of HAN concentrations presented an increase between >12-48 hours, which is then slightly reduced until 106 hours. This was expected, since higher water temperatures facilitated chemical reactions and therefore enhanced hydrolysis of HAN in the networks (Shi et al. 2017). On the contrary, during the sampling round with the coldest water temperature (*Round 2-winter*) there was no reduction observed, since the low temperatures possibly minimised chlorine consumption and delayed hydrolysis of HANs. The most unexpected pattern though was observed during the spring round (*Round 3*), where concentrations decreased until the location of medium water age (A-L2) and then increased until the location with the longest water age (A-L3). According to Glezer et al. (1999), haloacetonitriles are

unstable in alkaline conditions, and the pH 7.6 reported in A-L2 was the highest reported in the distribution network, so there is high chance these hydrolysed in a quicker rate. In the distribution network of water treatment **B** (*Table 5.3*), mean HAN concentrations were reported to be 3.0 µg/L, 5.0 µg/L and 5.2 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. In two of the four sampling rounds (*Round 2 & Round 4*), concentrations increased considerably until the location with medium water ages (24-48 hours), and then slightly decreased until 72-106 hours. The same pattern was observed in A WTW but during the months with high water temperatures registered, such as Round 4, which possibly resulted in faster rate of in situ reactions, with that of HAN hydrolysis at high water ages more prevalent than that of chlorine consumption. However, during Round 2 (*winter*) the pH was neutral in B-L1 and B-L2 and then became alkaline in distribution reaching a value of pH 7.6 in B-L3 and thus degradation occurred earlier. The pH increase may be influenced by several chemical, physical and biological factors in distribution systems of high retention times, through contact with specific pipe materials (e.g. cement or/and asbestos cement) or pipe corrosion products (Kirmeyer et al. 2000; Health Canada 2014).

Also, the bromide was an important factor in the speciation of haloacetonitriles, as it promoted the formation of the brominated species. The most predominant HAN species found in both chlorinated networks (A and B) were dibromoacetonitrile (DBAN), followed by bromochloroacetonitrile (BCAN), that indicated the abundant presence of brominated species (*Figure 5.3*). It is noteworthy though that contrary to all other sampling rounds where brominated species are more abundant, in sampling Round 4 (*summer*) chlorine-containing species, and especially TCAN were more dominant in WTW A and in the location closest to the treatment works of WTW B. The most possible explanation is that due to algae blooms, which are known to increase HAN formation (Fang et al. 2010; Yang et al. 2011) and were reported in these supply systems during that period, chlorine dosing was significantly higher in the treatment works to achieve the appropriate residual, something that was confirmed with the chlorine demand that these water samples presented during the SDS tests. The higher chlorine doses altered the chlorine to bromine ratio and favoured the formation of more chlorinated HANs. This impacted the speciation of THMs and HAAs as well, but to a lesser extent as it is shown in the speciation diagrams (*Figure 5.1 & Figure 5.2*).

Even though the results of this survey are indicative of HAN concentrations in distribution, the analysis identified only five of the nine species and therefore total concentrations are anticipated to be higher in reality. Nevertheless, the HAN concentrations observed in this study were safely below the guideline values for DBAN (70 µg/L) and DCAN (20 µg/L) recommended by the World Health Organisation (WHO 2004).

Overall, it was observed that the total HAN concentrations generated in the early stages of distribution are similar or slightly higher (by 0.4-2.5 µg/L) at the final stages, regardless of the intermediate increases and decreases. The fluctuations which occurred are mainly linked with the water quality parameters such as pH and water temperature, that impacted HAN stability, however there is no seasonal effect.

#### **5.1.1.4 Haloacetamides (HAcAms) in chlorinated systems**

This study included nine haloacetamides (HAcAms), which belong to the nitrogenous DBP group. Haloacetamides are believed to be more genotoxic and cytotoxic than the regulated DBPs (Bull et al. 2001; Plewa et al. 2008), yet there is only sparse information about the typical concentrations of many of these compounds in tap water, the mechanisms by which they are formed during water treatment/distribution, or their ultimate health significance in human populations. The results of this study included for the first time such a large number of HAcAm species and constitutes the most detailed and comprehensive database of HAcAms occurrence in the UK. Concerning their formation, literature suggests that HAcAms are primarily present in distribution networks as hydrolysis degradation products of HANs (Glezer et al. 1999; Reckhow et al. 2001). However, recent publications argue that these compounds may also form independently of HANs, and therefore should be treated as a standing DBP group with individual formation pathways and different precursors (Huang et al. 2012; Nihemaiti et al. 2016; Sfynia et al. 2016; Chu et al. 2016).

**Tables 5.1** and **5.2** summarise the median values of HAcAms identified in the selected downstream locations during the four seasonal sampling rounds in WTW A and B, respectively. In WTW A system, HAcAms are generally slightly increased with increasing water age in distribution networks. In more detail, total median HAcAm concentrations in WTW A were reported to be 2.5 µg/L, 3.5 µg/L and 4.4 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. The maximum concentration observed was 9.2 µg/L and was identified in the distribution location with the highest water age during Round 4 (*summer*). Even though during this sampling round, the highest water temperature was measured (22°C), HAcAms did not present any seasonal dependence, therefore these high concentrations are most likely due to the algal blooms in WTW A during the sampling period (Zhang et al. 2017). So, one of the first key messages were that HAcAms, as well as HANs formation, depended considerably on the characteristics of the organic matter in the water. The increases of HAcAms in WTW A, may be associated with the hydrolysis of HANs (Glezer et al. 1999) during the same water ages but the consistency that these increases occurred, when HANs were also increased, indicated that HAcAms may have followed different formation pathway(s) as well. In **WTW B**, on the other hand, the fate of HAcAms in distribution followed

a different pattern than in WTW A, where mean HAcAms concentrations were reported to be 3.9 µg/L, 4.7 µg/L and 3.9 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. The maximum concentration observed was 6.7 µg/L reported in D-L2 (*Round 2-winter*) and the minimum was 3.2 µg/L reported in D-L3 (*Round 4-summer*). For comparison, in the US study where HAcAms were initially reported (Weinberg et al. 2002), the median and maximum concentrations of the sum of HAcAms were 1.4 µg/L and 7.4 µg/L respectively, similar to those observed here, though note that only three of the possible brominated and chlorinated HAcAms were quantified.

The above observations indicated that HAcAms formation in chlorinated systems did not present any seasonal or temporal dependence since high formation was reported during samplings with significantly different water temperatures, similar to the chloraminated systems. The absence of seasonal dependency indicated that unlike temperature, other parameters like precursor characteristics play a more important role in the formation of HAcAms. The intermediate fluctuations in total concentrations was likely related to the combined effect of HAcAm degradation and re-formation potentially from other precursors found in the network (Bond 2012; Chu et al. 2016). Besides, there is not significant link between the reduction of HANs and the increase of HAcAms, or the decrease of HAcAms and the subsequent increase of HAAs. This indicated that there was a high chance that HAcAms formed independently from HANs in chlorinated systems (Huang et al. 2012; Nihemaiti et al. 2016).

Moreover, the bromide content of the final waters determined the speciation of HAcAms, since HOBr is considered as more efficient halogen substitution agent than chlorine (Cowman and Singer 1996). However, it is surprising that even though WTW A presented bromide concentrations below the detection limits during all sampling rounds (<12 µg/L), the weight ratios of the bromine containing HAcAms species were higher than those of WTW B, ranging from 43-75% and 16-81%, in WTW A and B, respectively. This highlighted that the incorporation of bromide in DBPs was different between the two chlorinated plants since it depended on other differentiating factors rather than concentration itself (Amy et al. 1991); nature and/or concentration of precursors. According to Krasner et al. (2006) the yields of dihalogenated HAcAm species were expected to be higher than the trihalogenated ones, something that was observed in the selected chlorinated systems during all sampling rounds.

The absence of consistent trend in the behaviour of both N-DBP groups with water age, and the fact that their concentrations variations were minimally affected by the journey to the taps, indicated that these

species do not necessarily form in distribution. Besides, the results highlighted that possibly the most important formation factor is the nature and constituents of the water matrices.

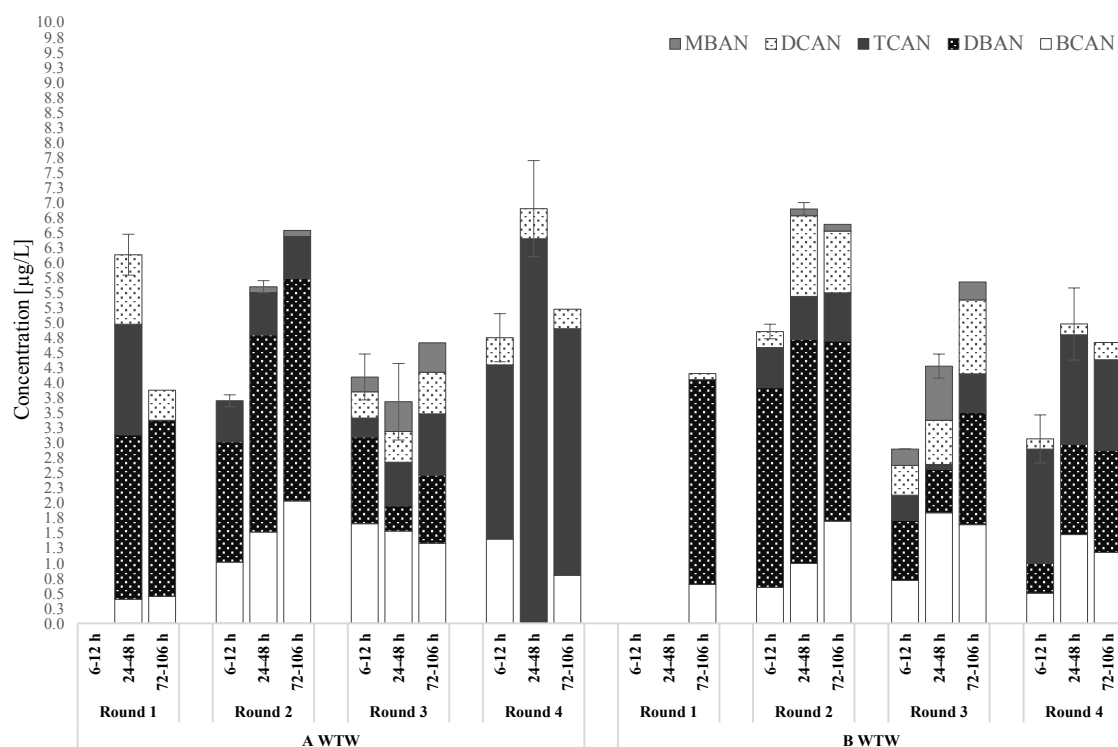


**Figure 5.3:** *HANs* speciation as a function of water age measured in *chlorinated systems A and B*. (Round 1-Sept 15', Round 2-Feb 16', Round 3-May 16', Round 4-Aug 16').

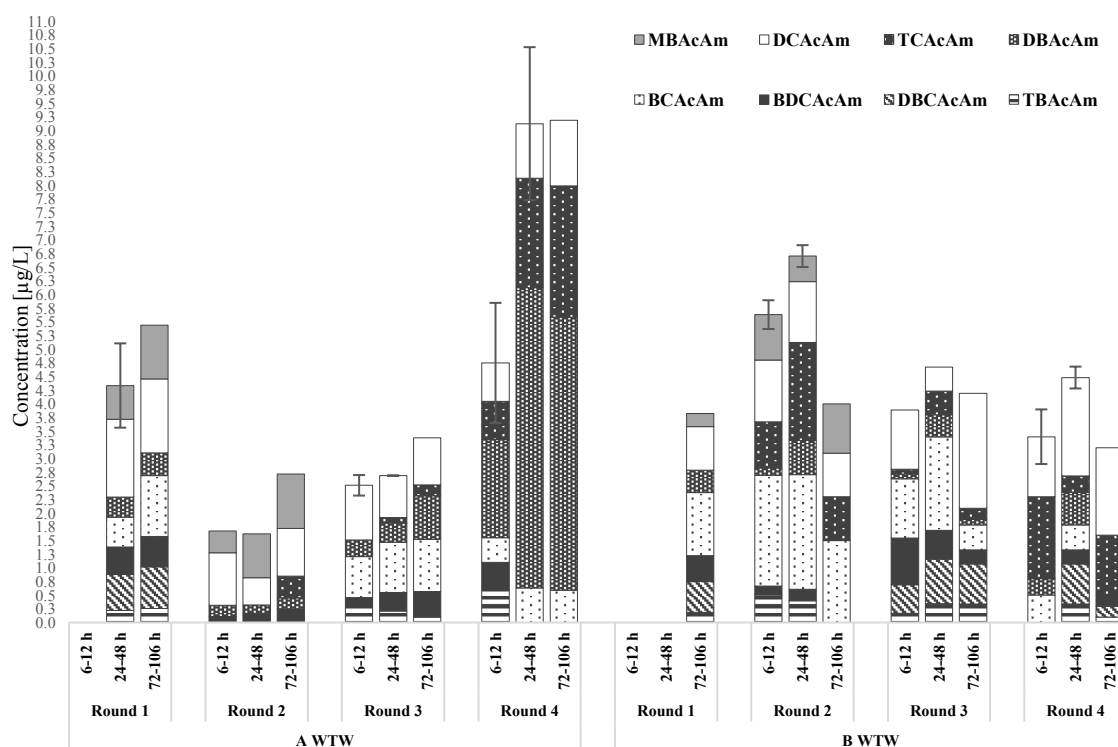


**Figure 5.4:** *HACams* speciation as a function of water age measured in *chlorinated systems A and B*. (Round 1-Sept 15', Round 2-Feb 16', Round 3-May 16', Round 4-Aug 16').

**Table 5.2:** Overview of DBP occurrence in distribution system **A** during all sampling rounds.

| WTW              | Round 1              |                  |     |                  |     |  | Round 2            |                  |      |                  |      |     | Round 3          |                  |      |                  |      |     | Round 4              |                  |      |                  |      |     |
|------------------|----------------------|------------------|-----|------------------|-----|--|--------------------|------------------|------|------------------|------|-----|------------------|------------------|------|------------------|------|-----|----------------------|------------------|------|------------------|------|-----|
|                  | September 15' ~ 17°C |                  |     |                  |     |  | February 16' ~ 8°C |                  |      |                  |      |     | May 16' ~ 14°C   |                  |      |                  |      |     | September 16' ~ 22°C |                  |      |                  |      |     |
| <b>A</b>         | L1                   | L2               |     | L3               |     |  | L1                 | L2               |      | L3               |      |     | L1               | L2               |      | L3               |      |     | L1                   | L2               |      | L3               |      |     |
|                  | [µg/L] <i>SD</i>     | [µg/L] <i>SD</i> |     | [µg/L] <i>SD</i> |     |  | [µg/L] <i>SD</i>   | [µg/L] <i>SD</i> |      | [µg/L] <i>SD</i> |      |     | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |      | [µg/L] <i>SD</i> |      |     | [µg/L] <i>SD</i>     | [µg/L] <i>SD</i> |      | [µg/L] <i>SD</i> |      |     |
| TTHMs            | 30.1                 | 43.7             | 0.9 | 57.9             | 6.9 |  | 25.6               | 0.0              | 36.0 | 0.0              | 52.9 | 0.4 | 29.0             | 0.8              | 45.2 | 1.4              | 60.8 | 3.2 | 38.7                 | 0.0              | 51.9 | 0.9              | 71.0 | 6.9 |
| THAAs            | -                    | 66.9             |     | 51.7             |     |  | 14.3               | 0.5              | 13.6 | 0.6              | 15.0 | 0.2 | 43.7             | 2.1              | 44.4 | 2.7              | 41.1 | 5   | 58.3                 | 0.5              | 61.2 | 0.6              | 55.1 | 0.2 |
| THANs            | -                    | 6.1              | 0.2 | 3.9              | 0.3 |  | 3.7                | 0.2              | 5.6  | 0.1              | 5.7  | 0.1 | 4.1              | 0.6              | 3.7  | 0.4              | 4.7  | 0.6 | 4.8                  | 0.2              | 6.9  | 0.1              | 5.2  | 0.1 |
| THAcAms          | -                    | 4.3              | 0.4 | 5.4              | 0.8 |  | 1.7                | 0.0              | 1.6  | 0.0              | 2.7  | 0.0 | 2.5              | 0.2              | 2.7  | 0.1              | 3.4  | 0.0 | 4.8                  | 0.5              | 9.1  | 0.5              | 9.2  | 0.0 |
| TOC <sub>a</sub> | 3.06                 |                  |     |                  |     |  | 3.69               |                  |      |                  |      |     | 3.55             |                  |      |                  |      |     | 3.40                 |                  |      |                  |      |     |
| Br <sub>b</sub>  | <12                  |                  |     |                  |     |  | <12                |                  |      |                  |      |     | <12              |                  |      |                  |      |     | <12                  |                  |      |                  |      |     |

L1: 6-12 hours      L2: 24-48 hours      L3: 72-106 hours

a: It was measured in the finished water of the WTW in mg/L C.

b: This value is calculated by the water utility in the finished water in µg/L.

**Table 5.3:** Overview of DBP occurrence in distribution system B during all sampling rounds.

| WTW                          | Round 1              |                  |                  |     | Round 2            |                  |                  |     |      |     | Round 3          |                  |                  |     |      |     | Round 4              |                  |                  |     |      |     |
|------------------------------|----------------------|------------------|------------------|-----|--------------------|------------------|------------------|-----|------|-----|------------------|------------------|------------------|-----|------|-----|----------------------|------------------|------------------|-----|------|-----|
|                              | September 15' ~ 17°C |                  |                  |     | February 16' ~ 8°C |                  |                  |     |      |     | May 16' ~ 14°C   |                  |                  |     |      |     | September 16' ~ 22°C |                  |                  |     |      |     |
| B                            | L1                   | L2               | L3               |     | L1                 | L2               | L3               |     |      |     | L1               | L2               | L3               |     |      |     | L1                   | L2               | L3               |     |      |     |
|                              | [µg/L] <i>SD</i>     | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |     | [µg/L] <i>SD</i>   | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |     |      |     | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |     |      |     | [µg/L] <i>SD</i>     | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |     |      |     |
| TTHMs                        | 31.4                 | 49.7             | 57.7             | 0.6 | 20.8               | 0.4              | 31.8             | 0.5 | 42.0 | 0.2 | 26.4             | 1.8              | 39.3             | 0.3 | 53.6 | 0.5 | 37.1                 | 0.6              | 49.3             | 3.5 | 65.9 | 4.1 |
| THAAs                        | -                    | -                | 59.4             |     | 10.6               | 0.2              | 9.8              | 0.3 | 12.2 | 0.1 | 30.0             | 0.7              | 29.4             | 0.3 | 34.4 | 0.1 | 32.5                 | 3.8              | 38.2             | 4.6 | 34.6 | 0.1 |
| THANs                        | -                    | -                | 4.2              | 0.8 | 4.9                | 0.2              | 6.9              | 0.1 | 6.6  | 0.1 | 2.9              | 0.0              | 4.3              | 0.0 | 5.7  | 0.2 | 3.1                  | 0.1              | 5.0              | 0.7 | 4.7  | 0.6 |
| THAcAms                      | -                    | -                | 3.8              | 0.2 | 5.6                | 0.1              | 6.7              | 0.3 | 4.0  | 0.2 | 3.9              | 0.0              | 4.7              | 0.0 | 4.2  | 0.0 | 3.4                  | 0.1              | 4.5              | 0.5 | 3.2  | 0.4 |
| TOC <sub>a</sub>             | 3.8                  |                  |                  |     | 3.6                |                  |                  |     |      |     | 4.2              |                  |                  |     |      |     | 3.7                  |                  |                  |     |      |     |
| Br <sup>-</sup> <sub>b</sub> | <12                  |                  |                  |     | 18.3               |                  |                  |     |      |     | <12              |                  |                  |     |      |     | 12.0                 |                  |                  |     |      |     |

L1: 6-12 hours      L2: 24-48 hours      L3: 72-106 hours

a: It was measured in the finished water of the WTW in mg/L C.

b: This value is calculated by the water utility in the finished water in µg/L.

### 5.1.2 In chloraminated water supply systems

Two of the distribution systems studied used *in-line* chloramines as the final disinfectant, and are designated as **C** and **D**. *Table 5.4* and *Table 5.5* present the results of THMs, HAAs, HANs and HAcAms total concentrations obtained in the selected downstream locations (L1, L2, L3), of chloraminated treatment works C and D, respectively, during all seasonal sampling rounds together with the TOC and bromide measurement of the final water in each treatment works. A more detailed database can be found in *Appendix B (B.9-B.16)*.

#### 5.1.2.1 Trihalomethanes (THMs) in chloraminated systems

Trihalomethanes in the distribution system of the chloraminated systems (*C&D*) were increasing as water age increased during all sampling rounds, a pattern that was expected. In **WTW C**, mean THM concentrations in WTW C were reported to be 17.0 µg/L, 26.7 µg/L and 34.9 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. The maximum concentration observed was 37.1 µg/L and was identified in the distribution location with the highest water age (C-L3) during Round 1 (*autumn*), closely followed by 36.9 µg/L observed in the same location during Round 4 (*summer*), whereas the minimum was 15.6 µg/L and was observed in Round 2 (*winter*). The water temperature of the systems that was clearly related with seasonality was found to be a key factor in the formation of THMs in chloraminated systems, as well. The increases in THM concentrations from the first and the last downstream location were important and consistent, since the concentrations in C-L1 were more than doubled (*mean*: 51.9 %) in most of the sampling rounds until water reached C-L3. In **WTW D**, THMs concentrations also increased with water age, with mean concentrations of 20.5 µg/L, 27.1 µg/L and 33.8 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations, with seasonal variations. Unlike all other systems selected, the water ages identified by modelling, in WTW D was not exceeding 72 hours, and thus D-L3 was falling into a range of 48-72 hours. Nevertheless, the possible lower water ages in this system did not favour the limitation of THM levels in the distribution network, since there were several cases where THMs were higher between a range of 48-72 hours in WTW D, than in 72-106 hours in WTW C. Indeed, the TOC in the water matrix of WTW D was higher than that of WTW C, which is linked to the inefficiency of the treatment processes implemented to remove organic precursors in the treatment works. The maximum concentration observed was 36.9 µg/L, identified in the distribution location with the highest water age (D-L3) during Round 1 (*autumn*), followed by 33.6 µg/L observed in the same location during Round 4 (*summer*), whereas the minimum was 15.6 µg/L, observed in Round 3 (*spring*). It is known though that

chloramines are less reactive than chlorine (Kirmeyer et al. 2000), and subsequently the rate by which THMs were increased was expected to be lower than the rate calculated during chlorination. Even though this was the case in WTW D, it was not also observed in WTW C. The THM formation rate in C WTW was either similar or even higher than that of the chlorinated systems (especially between C-L1 and C-L2). The assessment of water quality parameters in this system, such as pH, bromide levels, TOC and SUVA was insufficient to explain this trend. It appeared that this trend might have been related to the hydraulic conditions that existed in this distribution system, since even though it was the longest network it presented similar water ages than the shorter ones, indicating faster water transportation and possibly elevated mixing. Generally, trihalomethanes in the chloraminated systems (C&D) occurred in lower concentrations than in the chlorinated systems, but since each plant had different raw water characteristics, a direct comparison was not possible through the actual distribution samples. For this reason, separate tests were performed to assess the impact of alternative disinfection method in each system that can be found in *Chapter 5.3.*. The results from the chloraminated actual distribution networks indicated that THMs concentrations never exceeded the internal limits ( $<50 \mu\text{g/L}$ ) set by water utilities, even during sampling rounds with high water temperatures. Concerning the THM speciation, **Figure 5.5** illustrates the development of the different THM species in both C and D WTW over a period of four sampling rounds. One of the main differences between the two chloraminated systems was the level of bromide, which had a considerable impact on the formation of chloroform and bromine-containing species; bromide in WTW C was approximately four times higher than in WTW D. Consequently, in WTW C the bromide-containing species constituted the 76.2-94.0% of the total THMs levels, in all downstream locations, with the most abundant species being dibromochloromethane. On the other hand, in WTW D the weight fraction ratio of chloroform and bromide-containing was very similar (48.1:51.9), as bromide incorporation was reduced due to low bromide levels, with the most dominant species that of chloroform.

### 5.1.2.2 Haloacetic acids (HAAs) in chloraminated systems

Haloacetic acids results in the chloraminated systems (C&D) indicated that there were no consistent trends throughout the distribution network, with the exception of the locations with the highest water ages, where decrease in HAA concentrations occurred in WTW D and in three of the four sampling rounds in WTW C. When a decrease in HAA concentration was observed, usually between L2 and L3, the differences between the highest HAAs concentration and the concentration measured at C-L3 (72-106 hours) or D-L3 (48-72 hours) ranged 10-53% and 13.7-81.6%, respectively. These ranges are also confirmed by Baribeau et al. (2006) in HAAs occurrence in chloraminated distribution networks, with reported average ranges between 23-85%. In WTW C the maximum HAAs concentration reported was 53.7 µg/L in C-L2 (*Round 1*) and the minimum 14.3 µg/L in C-L1 (*Round 3*), whilst in WTW D the maximum concentration was 53.2 µg/L in D-L2 (*Round 4*) and the minimum 9.5 µg/L in D-L3 (*Round 1*). In general, in both chloraminated systems tri- and di-halogenated species accounted for most of HAAs concentrations. As mentioned above, the concentration decreases occurred in the downstream locations with the highest water ages that presented lower chloramines residuals (<0.5 mg/L), which suggested HAAs degradation. The decreases in HAA levels were basically due to the loss in mono- and di-haloacetic acids, which are reported to be the most biodegradable species, whereas tri-halogenated are the ones remained in L3. Furthermore, if a marker value of 40 µg/L was set, individual total concentrations exceeded this concentration during two of the four sampling rounds (*Round 1 & 4*) in both chloraminated systems, in the locations with the lowest and medium water ages (*L1 and L2*). Once more the concentration of the regulated HAAs (HAA5) represented 36.8-85.0% (*median 64.9%*) and 52.7-78.9% (*median 59.7 %*), for WTW C and D, respectively. It is noteworthy, that HAA5 represented less than 50 percent of total HAAs formed in WTW C in several locations and sampling rounds; this was linked to the increased level of brominated species, due to high bromide levels, that are not represented by HAA5. **Figure 5.6**, presents the total HAAs speciation as a function of the water age ranges identified in the chloraminated water works. Generally, bromide incorporation was high in the C WTW, which was anticipated from literature (Weinberg et al. 2002; Krasner et al. 2008) due to the relative high bromide levels (*median: 82 µg/L*) reported during all sampling rounds. Bromine-containing species in C WTW represented 56.5-85.8% of the total HAAs in three of the four sampling rounds (*Round 1, 3 & 4*), with the most abundant DBAA. Yet, during Round 2 chlorine-containing HAAs were dominating in all downstream locations, regardless the high bromide concentrations. This trend was surprising and contradictory with the other observations in the same system, however it has been reported by Cowman

and Singer (1996) with bromide levels of 100 µg/L resulted in only 10% generation of brominated HAAs. Also, in Ates et al. (2007) no formation shift was observed and the formation of chlorinated outweighed the brominated ones in waters with bromide ranging 60–110 µg/L. In WTW D, the distribution between the chlorinated and brominated species was more balanced with an average ratio 45.9:54.1 (*chlorinated: brominated*), since bromide levels were significant lower, with the most abundant species being TCAA. The weight fractions of bromine-containing HAAs followed numerous patterns with increasing water age in both chloraminated networks; decreased, increased or remained stable, linked with the combining effect of HAAs degradation and slower chloramine reactivity.

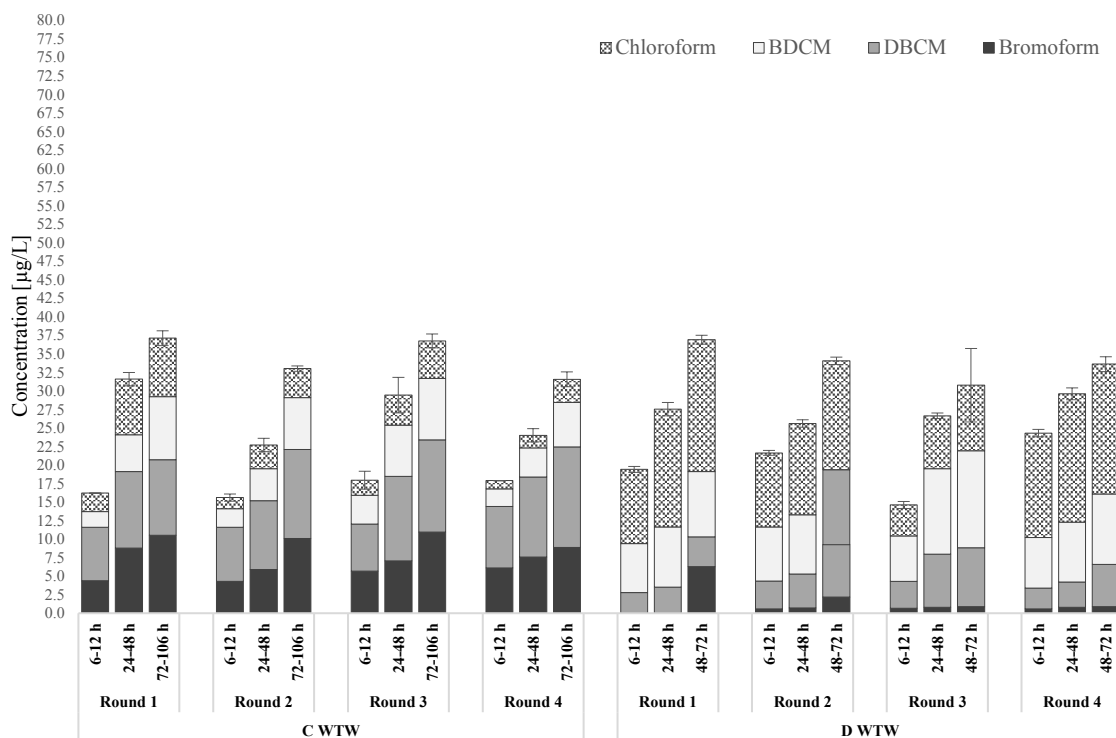


**Figure 5.5:** THM speciation as a function of water age measured in chloraminated systems C and D. (Round 1-Oct 15', Round 2-Mar 16', Round 3-Jun 16', Round 4-Sep 16').

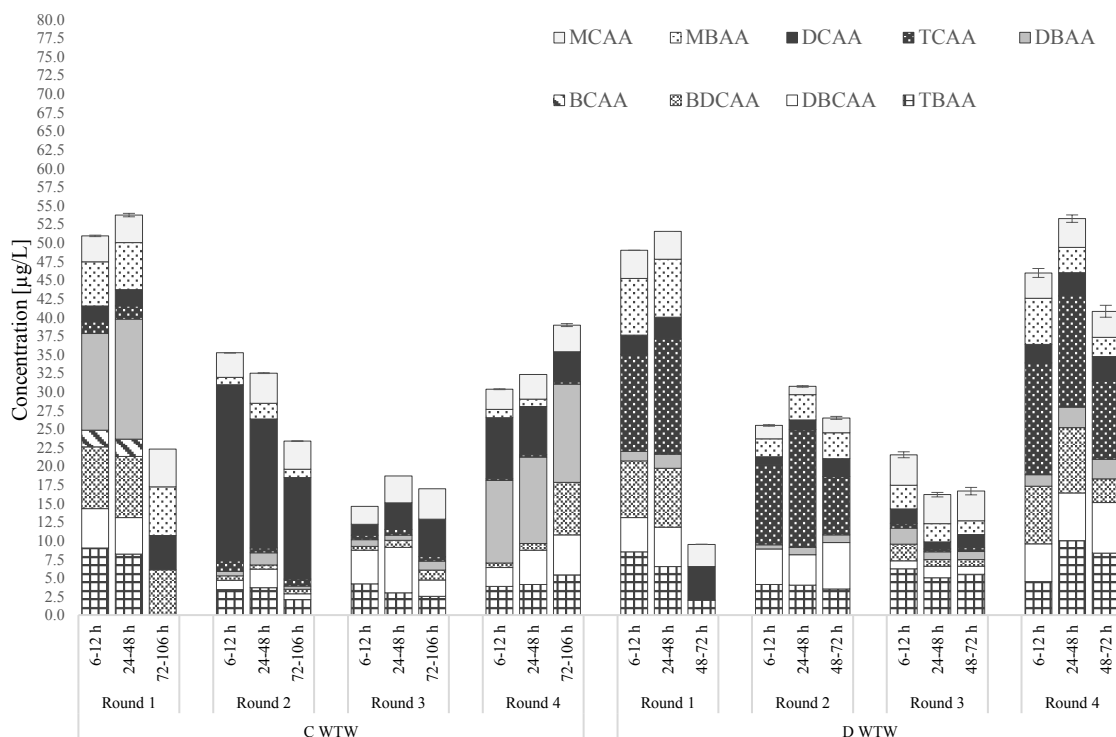


**Figure 5.6:** HAA speciation as a function of water age measured in chloraminated systems C and D (Round 1-Oct 15', Round 2-Mar 16', Round 3-Jun 16', Round 4-Sep 16').

### 5.1.2.3 Haloacetonitriles (HANs) in chloraminated systems

In the chloraminated distribution systems sampled (C and D), HANs were reported in slightly lower concentration than HAcAm concentrations during most of the sampling rounds. When these concentrations were compared against those of THMs and HAAs, HANs occurred in significantly lower amounts, and represented approximately 5% of the mass of total THMs and HAAs on a median basis, whereas HAcAms represented 13.5%. Although, HAcAms reported a maximum of 50% of HAA generation at one location (D-L3) in Round 1 where HAAs were relatively low. To the author's knowledge, though HANs have been previously reported to represent low mass percentages in chlorinated systems (Oliver 1983), such information concerning chloraminated systems was not found in the literature. In WTW C and D systems HANs were considerably lower than in the chlorinated ones (Templeton et al. 2012), whereas the effect of using chloramines as a disinfectant was less pronounced than for HAcAms. The median concentration from actual distribution locations was 1.5 µg/L for HANs and 3.8 µg/L for HAcAms. A survey that was carried out in Scotland included four HANs, for which median levels in chloraminated waters were reported to be very similar at 1.3 µg/L (Goslan et al. 2009).

The HAcAms concentrations identified in this study were slightly higher than those detected from the previous nationwide occurrence survey in England (Templeton et al. 2012), in which only three HAcAms were reported with mean concentrations of 1.5 µg/L. In more detail, in the chloraminated distribution system of C WTW median HAN concentrations were reported to be 1.1 µg/L, 1.0 µg/L and 1.2 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. Indeed, the occurrence was very low, and the fluctuations observed were considered minimal to form a trend with water age; in two of the sampling rounds (1&3) concentrations constantly increased with time and in the other two sampling rounds (2&4) decreased until the location with the medium water age (C-L2) and then increased again until C-L3. Since the total HANs levels are low, the increases observed in locations with medium and higher water ages were due to the slow formation rate of brominated species that were detected, as in locations with low water age these were below the detection limits. Once more, the HANs decreases between >12-24 hours are mainly related to faster hydrolysis rate, due to the alkaline water environment (pH=8) during these rounds, that impacted the stability of these compounds (Glezer et al. 1999). In the distribution network of water treatment works D, median HAN concentrations were reported to be 1.8 µg/L, 1.8 µg/L and 1.9 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. The behavioural pattern of HANs in WTW D, was not conclusive in relation with water age, since all possible scenarios occurred. In

two of the four sampling rounds (Round 3 & Round 4), concentrations increased considerably until the location with water ages ranging 24-48 hours, and then were slightly decreased until 72-106 hours, whereas in Round 1 (*autumn*) concentrations were reported to constantly increase with water age. Unlike the other rounds, in Round 2 (*winter*) hydrolysis occurred in lower water ages (DCAN decreased) and was not observed in combination with pH alteration in distribution. In any case, the limited formation did not provide conclusive trends and the fluctuations may be also related to analytical method deviations.

Bromide incorporation in haloacetonitriles not only promoted the formation of brominated species but also increased the compound stability (Glezer et al. 1999). The most abundant HAN species found in chloraminated WTW C was dibromoacetonitrile (DBAN), due to its highest bromide concentration (*median*: 82 µg/L), whereas in WTW D was dichloroacetonitrile (DCAN), due to its lowest bromide concentration observed (*median*: 19.9 µg/L). The speciation and the trends are illustrated in **Figure 5.7**. Even though the relationship between high bromide and high DBPs occurrence has been widely discussed (Cowman and Singer 1996; Obolensky and Singer 2008; Templeton et al. 2010; Bond et al. 2011; Hua and Reckhow 2012) and confirmed in the formation of THMs and HAAs in this study, in the case of HANs bromide affected only the speciation but not the occurrence levels in chloraminated systems. In more detail, even though the median percentage of brominated THMs and HAAs was respectively, 79% and 62%, the median percentage of brominated HANs was only 33%. This demonstrated that the relative bromide incorporation for different DBP groups may vary, which was essentially linked to site-specific differences in precursor characteristics and oxidation conditions. Needless to mention that the HAN concentrations observed in chloraminated systems were safely below the guideline values for DBAN (70 µg/L) and DCAN (20 µg/L) recommended by the World Health Organisation (WHO 2004). Overall, it is observed that the total HAN concentrations were not affected by seasonal variations and the concentrations reported in the early stages of distribution are similar or slightly higher (by 0.1-0.8 µg/L) at the final stages, regardless of the intermediate minimal fluctuations.

#### **5.1.2.4 Haloacetamides (HAcAms) in chloraminated systems**

**Table 5.4** and **5.5** summarise the mean values of HAcAms identified in the selected downstream locations during the four seasonal sampling rounds in WTW C and D, respectively. The median concentration from actual chloraminated distribution locations was 3.8 µg/L for HAcAms, marginally lower than that in chlorination systems (4.0 µg/L). In both WTW C and D systems, HAcAms are generally increased with increasing water age in distribution networks until the location with the medium water age (L2) and then

decreased until the location with the highest water age (L3). In more detail, median HAcAm concentrations in WTW C were reported to be 3.5 µg/L, 4.2 µg/L and 4.0 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. The maximum concentration observed was 4.7 µg/L, followed by 4.6 µg/L, both identified in the distribution location with the medium water age during Round 3 (*spring*) and 4 (*summer*), respectively. In WTW D, mean HAcAms concentrations were reported to be 3.2 µg/L, 4.0 µg/L and 4.3 µg/L, in the low (L1), medium (L2) and high (L3) water age downstream locations. The maximum concentration observed was 5.7 µg/L reported in D-L3 (*Round 2-winter*) and the minimum was 3.0 µg/L reported in D-L1 (*Round 3-spring*). From the above observations, it was clear that HAcAms formation in chloraminated systems did not present any seasonal dependence since high formation was reported during samplings with significantly different water temperatures, similarly to the chlorinated systems. Therefore, the higher concentrations observed in L2 were related to the subsequent hydrolysis of these compounds after 48 hours, which was coherent with the relative increases of HAAs at the same water age, but not that coherent with the reductions of HANs. The latter indicated that HAcAms may form independently from HANs during the early stages of water disinfection in chloraminated systems as well. The absence of seasonal dependency indicated that unlike temperature, other parameters like precursor characteristics played a more important role in the formation of HAcAms.

Furthermore, the weight ratios of bromine containing HAcAms species identified in WTW C was significantly higher than that of the chlorinated ones ranging from 66.3-93.6% during the sampling rounds. The fluctuations of the brominated species followed the exact same pattern as the HAcAms concentration fluctuations that showed that the degradation observed was mainly affecting the brominated HAcAms. On the other hand, in WTW D (*Br median: 19.9 µg/L*), where bromide levels were significantly lower than in WTW C (*Br median: 82 µg/L*), still brominated species represented the majority of weight fraction with a lower range (54.3-77%). The latter highlighted the high bromide incorporation in HAcAm even in systems with relatively low bromide levels (< 20 µg/L), which is important when considering mitigation strategies for HAcAms levels. In addition, it was noteworthy that in both chloraminated systems, regardless of the bromide level, DCAcAm occurred at similar levels to DCAN, with respective median values of 0.5 µg/L and 0.6 µg/L in WTW C, and respective median values of 1.4 µg/L and 1.1 µg/L in WTW D. Also, the dihalogenated representatives of the HAcAms group were found at higher levels than the trihalogenated ones. Both these observations have been previously noted by Krasner et al. (2006) in the N-DBP occurrence study in the US.

It is interesting though, that regardless of the seasonal and temporal variations and the disinfection method applied in the four distribution systems selected, HANs and HAcAms presented similar levels during all sampling rounds. All these results from the actual distribution systems indicated the weight of each factor in the formation of THMs, HAAs, HANs and HAcAms in chlorinated and chloraminated systems. The preliminary conclusions from the actual networks are important but not enough to make recommendation on how these systems need to operate to mitigate DBP formation, since several parameters such as water age ranges provided ambiguity in the results. Therefore, a tool to simulate DBPs formation (SDS tests) under the same conditions was implemented and validated as a core work package of this research.

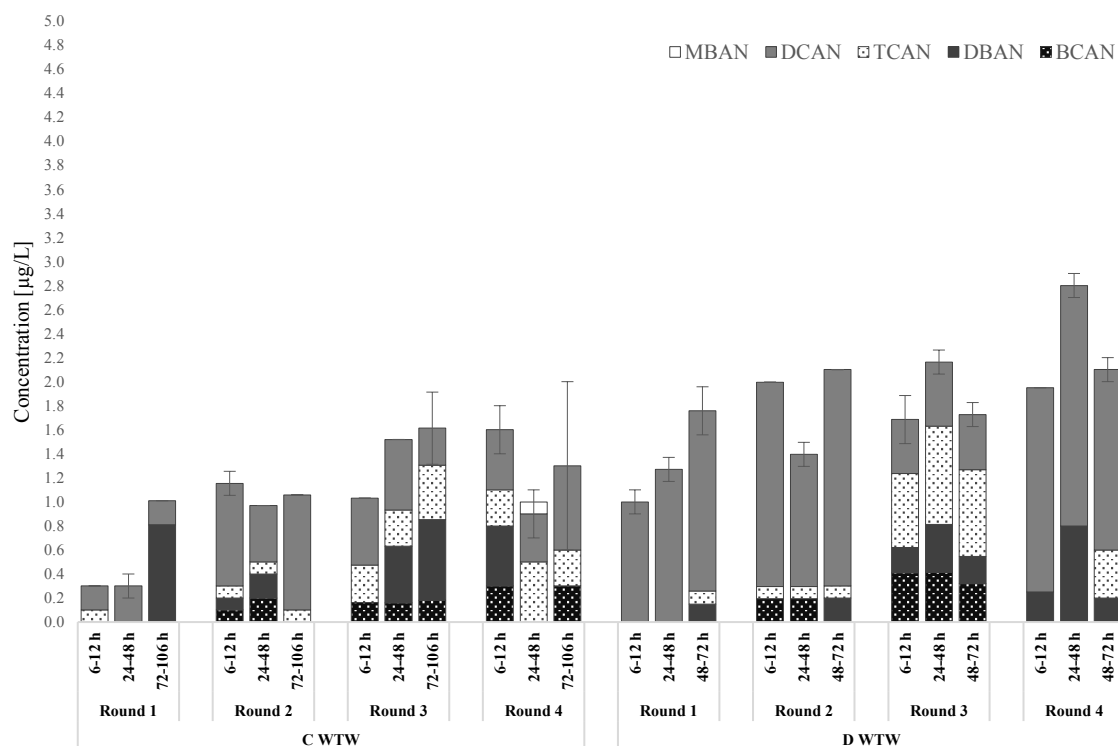


**Figure 5.7:** HANs speciation as a function of water age measured in chloraminated systems C and D (Round 1-Oct 15', Round 2-Mar 16', Round 3-Jun 16', Round 4-Sep 16')

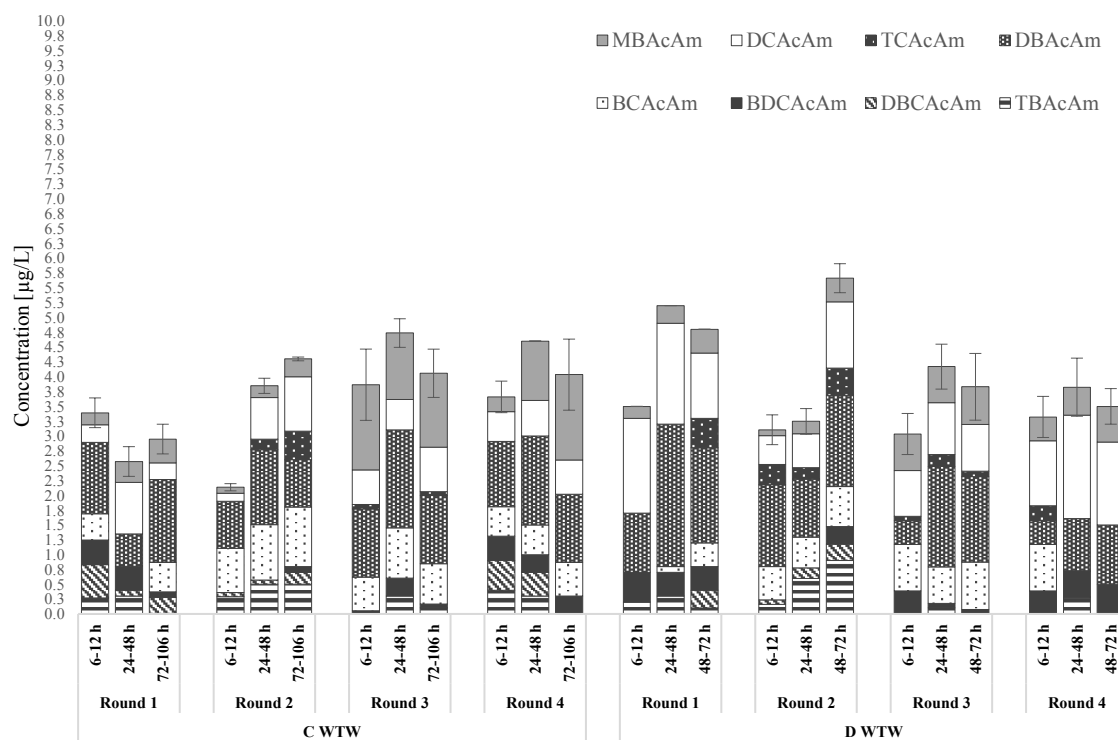


**Figure 5.8:** HAcs speciation as a function of water age measured in chloraminated systems C and D (Round 1-Oct 15', Round 2-Mar 16', Round 3-Jun 16', Round 4-Sep 16')

**Table 5.4:** Overview of DBPs occurrence in distribution system C during all sampling rounds.

| WTW                          | Round 1            |                  |      |                  |      |     | Round 2          |                  |      |                  |      |     | Round 3          |                  |      |                  |      |     | Round 4              |                  |      |                  |      |     |
|------------------------------|--------------------|------------------|------|------------------|------|-----|------------------|------------------|------|------------------|------|-----|------------------|------------------|------|------------------|------|-----|----------------------|------------------|------|------------------|------|-----|
|                              | October 15' ~ 14°C |                  |      |                  |      |     | March 16' ~ 8°C  |                  |      |                  |      |     | June 16' ~ 17°C  |                  |      |                  |      |     | September 16' ~ 22°C |                  |      |                  |      |     |
| C                            | L1                 | L2               |      | L3               |      |     | L1               | L2               |      | L3               |      |     | L1               | L2               |      | L3               |      |     | L1                   | L2               |      | L3               |      |     |
|                              | [µg/L] <i>SD</i>   | [µg/L] <i>SD</i> |      | [µg/L] <i>SD</i> |      |     | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |      | [µg/L] <i>SD</i> |      |     | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |      | [µg/L] <i>SD</i> |      |     | [µg/L] <i>SD</i>     | [µg/L] <i>SD</i> |      | [µg/L] <i>SD</i> |      |     |
| TTHMs                        | 16.2               | 0.0              | 31.6 | 0.9              | 37.1 | 1.0 | 15.6             | 0.5              | 22.7 | 0.9              | 33.0 | 0.4 | 17.9             | 1.2              | 29.4 | 2.4              | 36.7 | 0.9 | 17.9                 | 0.0              | 24.0 | 0.9              | 31.6 | 1.0 |
| THAAs                        | 50.9               | 1.9              | 22.3 | 0.4              | 7.6  | 0.1 | 35.2             | 1.4              | 32.5 | 0.9              | 23.4 | 0.7 | 14.6             | 0.9              | 18.7 | 1.1              | 17.0 | 1.1 | 30.3                 | 0.9              | 32.3 | 1.1              | 38.9 | 1.1 |
| THANs                        | 0.2                | 0.0              | 0.3  | 0.0              | 1.0  | 0.0 | 1.2              | 0.1              | 1.0  | 0.0              | 1.1  | 0.0 | 1.0              | 0.0              | 1.5  | 0.1              | 1.6  | 0.1 | 1.6                  | 0.0              | 1.0  | 0.1              | 1.3  | 0.1 |
| THAcAms                      | 3.8                | 0.3              | 2.6  | 0.3              | 1.9  | 0.3 | 2.1              | 0.1              | 3.8  | 0.1              | 4.3  | 0.0 | 3.9              | 0.6              | 4.7  | 0.2              | 4.1  | 0.4 | 3.7                  | 0.3              | 4.6  | 0.7              | 4.0  | 0.6 |
| TOC <sub>a</sub>             | 3.3                |                  |      |                  |      |     | 3.5              |                  |      |                  |      |     | 3.2              |                  |      |                  |      |     | 3.9                  |                  |      |                  |      |     |
| Br <sup>-</sup> <sub>b</sub> | 82.0               |                  |      |                  |      |     | 85.1             |                  |      |                  |      |     | 76.0             |                  |      |                  |      |     | 80.0                 |                  |      |                  |      |     |

L1: 6-12 hours      L2: 24-48 hours      L3: 72-106 hours

a: It was measured in the finished water of the WTW in mg/L C.

b: This value is calculated by the water utility in the finished water in µg/L.

**Table 5.5:** Overview of DBPs occurrence in distribution system D during all sampling rounds.

| WTW              | Round 1            |                  |          |                  |  |  | Round 2          |                  |          |                  |  |  | Round 3          |                  |          |                  |  |  | Round 4              |                  |          |                  |  |  |
|------------------|--------------------|------------------|----------|------------------|--|--|------------------|------------------|----------|------------------|--|--|------------------|------------------|----------|------------------|--|--|----------------------|------------------|----------|------------------|--|--|
|                  | October 15' ~ 14°C |                  |          |                  |  |  | March 16' ~ 8°C  |                  |          |                  |  |  | June 16' ~ 17°C  |                  |          |                  |  |  | September 16' ~ 22°C |                  |          |                  |  |  |
| D                | L1                 | L2               |          | L3               |  |  | L1               | L2               |          | L3               |  |  | L1               | L2               |          | L3               |  |  | L1                   | L2               |          | L3               |  |  |
|                  | [µg/L] <i>SD</i>   | [µg/L] <i>SD</i> |          | [µg/L] <i>SD</i> |  |  | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |          | [µg/L] <i>SD</i> |  |  | [µg/L] <i>SD</i> | [µg/L] <i>SD</i> |          | [µg/L] <i>SD</i> |  |  | [µg/L] <i>SD</i>     | [µg/L] <i>SD</i> |          | [µg/L] <i>SD</i> |  |  |
| TTHMs            | 19.4 0.4           | 27.5 0.9         | 36.9 0.6 |                  |  |  | 21.6 0.3         | 25.6 0.5         | 34.1 0.5 |                  |  |  | 14.6 0.5         | 26.6 0.4         | 30.8 5.0 |                  |  |  | 24.3 0.5             | 29.6 0.8         | 33.6 1.0 |                  |  |  |
| THAAs            | 49.0 1.1           | 51.5 0.8         | 9.5 0.0  |                  |  |  | 25.5 0.8         | 30.7 0.9         | 26.5 0.7 |                  |  |  | 21.5 3.9         | 16.2 3.6         | 16.6 1.7 |                  |  |  | 45.9 1.1             | 53.2 0.8         | 40.8 0.3 |                  |  |  |
| THANs            | 1.0 0.0            | 1.3 0.1          | 1.8 0.0  |                  |  |  | 2.0 0.0          | 1.4 0.0          | 2.1 0.0  |                  |  |  | 1.7 0.1          | 2.2 0.1          | 1.7 0.1  |                  |  |  | 2.0 0.1              | 2.8 0.1          | 2.1 0.2  |                  |  |  |
| THAcAms          | 3.5 0.0            | 4.8 0.0          | 2.6 0.0  |                  |  |  | 3.1 0.3          | 3.2 0.2          | 5.7 0.2  |                  |  |  | 3 0.3            | 4.2 0.4          | 3.8 0.6  |                  |  |  | 3.3 0.3              | 3.8 0.5          | 3.5 0.0  |                  |  |  |
| TOC <sup>a</sup> | 2.8                |                  |          |                  |  |  | 2.8              |                  |          |                  |  |  | 1.8              |                  |          |                  |  |  | 2.8                  |                  |          |                  |  |  |
| Br <sup>-b</sup> | 13.2               |                  |          |                  |  |  | 19.9             |                  |          |                  |  |  | 26.4             |                  |          |                  |  |  | <12                  |                  |          |                  |  |  |

L1: 6-12 hours      L2: 24-48 hours      L3: 48-72 hours

a: It was measured in the finished water of the WTW in mg/L C.

b: This value is calculated by the water utility in the finished water in µg/L.

### 5.1.3 Correlations between DBPs and water quality parameters in actual distribution

There have been many attempts to investigate the relationship between the water quality parameters and the DBP levels with the aim to identify surrogate indicators and therefore predict the occurrence of other DBP without further analysis. The aim of this correlation, though, was essentially to further understand the interconnections and interdependencies of the various DBPs identified and water quality measurements, towards an improved understanding on how to control DBPs occurrence in distribution. In this study, Pearson correlation coefficient ( $r$ ) was calculated to examine potential correlations between water quality and DBP concentrations in actual chlorinated and chloraminated distribution systems (Tables 5.6 and 5.7) by including all the data separately for each disinfection practice. The fact that the water matrices sampled for this analysis stemmed from real water treatment works limited the variability of several water quality parameters such as pH and disinfectant residual, since these are controlled in situ to adhere to regulatory compliance. However, the sampling rounds were designed in a way to enable correlations with other parameters such as temperature, TOC, water age and of course between the various DBP groups.

As expected the most pronounced correlation in both chlorinated and chloraminated systems was that of total THMs with water age, with  $r$  values of 0.85 and 0.92, respectively. Another important correlation observed within these calculations that was discussed above was that of bromide and total N-DBPs concentrations in chlorinated systems ( $r=0.69$  HANs and  $r=0.70$  HAcAms), and that of bromide ( $<12-26.4$   $\mu\text{g/L}$ ) and only HAcAms concentrations in chloraminated systems ( $r=0.81$ ). This suggested that the bromide levels in water influenced the formation of both HANs and HAcAms in chlorinated distribution systems, whereas in chloraminated systems bromide was mainly incorporated in HAcAms without affecting the formation of HANs. Furthermore, literature suggests that HAcAms form from HANs hydrolysis, and can subsequently hydrolyse further to form HAAs (Glezer et al. 1999; Reckhow et al. 2001). Indeed, in chlorinated systems there is a similar correlation ( $r=0.65, 0.68, 0.74$ ) between these groups but primarily between their respective chlorinated species (**Table 5.6**). This indicated that the chlorine-containing species of these three DBP groups had high probability to be complementary, however this was not the case with their bromine-containing species. In chloraminated systems, on the other hand, correlation was observed only between the chlorine-containing HANs and HAcAms ( $r=0.85$ ), which indicated that HAAs levels observed are not due to HAcAms degradation, at least until the highest water age due to limited chloramines reactivity. Bromine-containing species presented different behaviour than chlorine-containing species since they differ stereochemically (Baribeau et al. 2006); stability of the

carbon-halogen bond increases with increasing electronegativity of the halogen ( $\text{Br} > \text{Cl}$ ), and the larger the bond dissociation energy, the stronger the bond. These trends suggested that even though HAAs, HAcAms and HANs were interrelated and shared the same precursors to some extent, however since there is no relative correlation between their total concentrations and/or their bromine-containing species, independent formation from different precursors was also highly probable. Bromine-containing species, obviously linked with bromide incorporation, correlated with the total concentrations of the majority of DBP groups both in chlorination and chloramination. This observation agreed with multiple surveys that have linked bromide concentration with increased levels of DBPs (Krasner et al. 1989; Hua and Reckhow 2012).

Concerning the other water quality parameters, even though literature often refers to TOC as important surrogate measurement for DBP formation, the TOC variation between the sampling rounds was statistically insignificant and therefore was unable to predict occurrence trends. In fact, the correlations between TOC, SUVA and DBP groups were very poor and thus were not considered as good indicators of regulated and unregulated DBPs occurrence in distribution systems. This observation concerning TOC and SUVA agreed with a report published by US EPA (2004) that argued that these two parameters ‘may be too generalised’ to accurately predict DBPs formation especially for regulatory purposes.

**Table 5.6:** Correlations\* between DBP groups and water quality parameters in actual chlorinated distribution systems (WTW A and B).

|                   | <i>Total<br/>THMs</i> | <i>CHCl<sub>3</sub></i> | <i>Br-THMs</i> | <i>Total<br/>HAAs</i> | <i>Cl-HAAs</i> | <i>Br-HAAs</i> | <i>Total<br/>HANs</i> | <i>Cl-HANs</i> | <i>Br-HANs</i> | <i>Total<br/>HAcAms</i> | <i>Cl-HAcAms</i> | <i>Br-HAcAms</i> |
|-------------------|-----------------------|-------------------------|----------------|-----------------------|----------------|----------------|-----------------------|----------------|----------------|-------------------------|------------------|------------------|
| Total THMs        |                       |                         |                |                       |                |                |                       |                |                |                         |                  |                  |
| CHCl <sub>3</sub> | <b>0.64</b>           |                         |                |                       |                |                |                       |                |                |                         |                  |                  |
| Br-THMs           | <b>0.97</b>           | 0.42                    |                |                       |                |                |                       |                |                |                         |                  |                  |
| Total HAAs        | <b>0.50</b>           | 0.43                    | 0.45           |                       |                |                |                       |                |                |                         |                  |                  |
| Cl-HAAs           | 0.41                  | 0.49                    | 0.33           | <b>0.83</b>           |                |                |                       |                |                |                         |                  |                  |
| Br-HAAs           | 0.48                  | 0.33                    | 0.45           | <b>0.94</b>           | <b>0.59</b>    |                |                       |                |                |                         |                  |                  |
| Total HANs        | 0.20                  | 0.14                    | 0.18           | -0.04                 | -0.04          | -0.03          |                       |                |                |                         |                  |                  |
| Cl-HANs           | 0.30                  | 0.48                    | 0.20           | 0.47                  | <b>0.65</b>    | 0.29           | <b>0.53</b>           |                |                |                         |                  |                  |
| Br-HANs           | -0.12                 | -0.36                   | -0.02          | -0.55                 | -0.73          | -0.37          | <b>0.56</b>           | -0.55          |                |                         |                  |                  |
| Total HAcAms      | 0.30                  | 0.49                    | 0.20           | 0.35                  | 0.41           | 0.26           | 0.46                  | <b>0.74</b>    | -0.28          |                         |                  |                  |
| Cl-HAcAms         | 0.33                  | 0.33                    | 0.29           | 0.09                  | 0.25           | -0.01          | 0.40                  | <b>0.68</b>    | -0.32          | <b>0.73</b>             |                  |                  |
| Br-HAcAms         | 0.21                  | 0.47                    | 0.10           | 0.42                  | 0.40           | 0.36           | 0.39                  | <b>0.61</b>    | -0.17          | <b>0.92</b>             | 0.41             |                  |
| Temperature       | 0.47                  | 0.30                    | 0.45           | <b>0.77</b>           | <b>0.85</b>    | <b>0.60</b>    | -0.14                 | <b>0.55</b>    | -0.76          | 0.40                    | 0.45             | 0.27             |
| pH                | 0.18                  | 0.21                    | 0.15           | 0.42                  | 0.34           | 0.47           | -0.30                 | -0.16          | -0.17          | -0.30                   | -0.32            | -0.25            |
| Bromide           | -0.68                 | -0.93                   | -0.65          | -0.99                 | -0.96          | -0.99          | <b>0.69</b>           | -0.45          | <b>0.84</b>    | <b>0.70</b>             | -0.34            | <b>0.81</b>      |
| UV                | 0.13                  | 0.01                    | 0.16           | 0.32                  | 0.33           | 0.31           | -0.09                 | 0.21           | -0.13          | -0.08                   | -0.13            | -0.03            |
| TOC               | -0.39                 | -0.26                   | -0.42          | -0.31                 | -0.28          | -0.32          | -0.48                 | -0.55          | 0.01           | -0.40                   | -0.35            | -0.37            |
| SUVA              | 0.16                  | -0.09                   | 0.24           | 0.26                  | 0.29           | 0.22           | -0.16                 | 0.46           | -0.29          | -0.12                   | 0.21             | -0.30            |
| Residual          | -0.63                 | -0.28                   | -0.68          | 0.15                  | 0.36           | -0.01          | 0.03                  | 0.32           | -0.34          | 0.03                    | 0.05             | 0.02             |
| Water age         | <b>0.85</b>           | 0.48                    | <b>0.85</b>    | 0.14                  | -0.04          | 0.22           | 0.36                  | 0.02           | 0.35           | 0.16                    | 0.15             | 0.13             |

\* Pearson product moment correlation coefficient

**Table 5.7:** Correlations\* between DBP groups and water quality parameters in actual chloraminated distribution systems (WTW C and D).

|                   | <i>Total<br/>THMs</i> | <i>CHCl<sub>3</sub></i> | <i>Br-THMs</i> | <i>Total<br/>HAAs</i> | <i>Cl-HAAs</i> | <i>Br-HAAs</i> | <i>Total<br/>HANs</i> | <i>Cl-HANs</i> | <i>Br-HANs</i> | <i>Total<br/>HAcAms</i> | <i>Cl-HAcAms</i> | <i>Br-HAcAms</i> |
|-------------------|-----------------------|-------------------------|----------------|-----------------------|----------------|----------------|-----------------------|----------------|----------------|-------------------------|------------------|------------------|
| Total THMs        |                       |                         |                |                       |                |                |                       |                |                |                         |                  |                  |
| CHCl <sub>3</sub> | 0.47                  |                         |                |                       |                |                |                       |                |                |                         |                  |                  |
| Br-THMs           | <b>0.67</b>           | -0.34                   |                |                       |                |                |                       |                |                |                         |                  |                  |
| Total HAAs        | -0.21                 | 0.22                    | -0.40          |                       |                |                |                       |                |                |                         |                  |                  |
| Cl-HAAs           | -0.15                 | 0.28                    | -0.40          | <b>0.51</b>           |                |                |                       |                |                |                         |                  |                  |
| Br-HAAs           | -0.15                 | 0.09                    | -0.24          | <b>0.87</b>           | 0.02           |                |                       |                |                |                         |                  |                  |
| Total HANs        | 0.24                  | <b>0.57</b>             | -0.22          | -0.21                 | 0.12           | -0.32          |                       |                |                |                         |                  |                  |
| Cl-HANs           | 0.18                  | <b>0.72</b>             | -0.42          | -0.01                 | 0.28           | -0.17          | <b>0.85</b>           |                |                |                         |                  |                  |
| Br-HANs           | 0.16                  | -0.18                   | 0.34           | -0.12                 | -0.23          | 0.02           | 0.24                  | -0.33          |                |                         |                  |                  |
| Total<br>HAcAms   | 0.41                  | 0.26                    | 0.22           | -0.24                 | -0.18          | -0.18          | 0.27                  | 0.33           | -0.07          |                         |                  |                  |
| Cl-HAcAms         | 0.35                  | <b>0.78</b>             | -0.29          | 0.21                  | 0.30           | 0.07           | 0.49                  | <b>0.68</b>    | -0.11          | 0.49                    |                  |                  |
| Br-HAcAms         | 0.23                  | -0.23                   | 0.44           | -0.42                 | -0.40          | -0.26          | -0.03                 | -0.09          | 0.00           | <b>0.81</b>             | -0.12            |                  |
| Temperature       | 0.09                  | 0.16                    | -0.03          | 0.40                  | -0.17          | <b>0.56</b>    | 0.11                  | 0.04           | 0.18           | 0.03                    | 0.11             | -0.04            |
| pH                | -0.45                 | -0.29                   | -0.24          | 0.31                  | 0.30           | 0.20           | 0.08                  | 0.10           | -0.12          | -0.19                   | -0.27            | -0.04            |
| Bromide           | -0.01                 | -0.78                   | <b>0.55</b>    | 0.07                  | 0.03           | 0.06           | -0.63                 | -0.77          | 0.27           | -0.35                   | -0.64            | -0.02            |
| UV                | -0.08                 | 0.33                    | -0.36          | 0.14                  | <b>0.64</b>    | -0.19          | 0.39                  | <b>0.64</b>    | -0.66          | 0.10                    | 0.27             | -0.05            |
| TOC               | 0.13                  | 0.07                    | 0.07           | 0.20                  | 0.40           | 0.01           | -0.43                 | -0.25          | -0.24          | -0.05                   | 0.02             | -0.07            |
| SUVA              | -0.30                 | -0.67                   | 0.38           | -0.17                 | -0.41          | 0.01           | 0.05                  | -0.24          | 0.22           | -0.35                   | -0.74            | 0.08             |
| Residual          | -0.25                 | -0.35                   | -0.02          | -0.06                 | -0.25          | 0.08           | -0.27                 | -0.39          | 0.18           | -0.69                   | -0.58            | -0.45            |
| Water age         | <b>0.92</b>           | 0.31                    | <b>0.72</b>    | -0.30                 | -0.18          | -0.24          | 0.17                  | 0.11           | 0.09           | 0.45                    | 0.25             | 0.35             |

\* Pearson product moment correlation coefficient

## 5.2 Occurrence of regulated and unregulated DBPs in SDS tests

Simulated distribution system tests were performed in all four selected water works to assess the potential of this tool to simultaneously predict the formation and behavior of THMs, HAAs, HANs and HAcAms in both chlorinated and chloraminated distribution systems. Once more the following chapters that elaborate the results from the SDS tests are organised by the type of disinfectant applied at the water works.

SDS tests were conducted with real final water matrices during all the seasonal sampling rounds, in parallel with actual distribution samples collection, to enable direct comparisons and validate this tool for HANs and HAcAms. The detailed database is presented in *Appendix B (B.1-B.8)*, however illustrative graphs and key tables of the findings can also be found in the following subchapters. SDS tests aim to simulate the *water quality*, *disinfectant residuals*, and *water ages* of a real distribution system, allowing easy sampling at prescribed time intervals for analysis of DBP formation. The pre-determined time intervals were 6, 12, 24, 48, 72 and 106 hours, to simulate the relative water age ranges identified by modeling the actual distribution networks of the selected water works. These tests are also a useful tool for considering the impact of potential changes to distribution practices, such as switching from chlorination to chloramination (*Chapter 5.3.1*). Furthermore, it has to be noted that HANs and HAcAms concentration scales in distribution systems and SDS tests were considerably lower than those of THMs and HAAs.

### 5.2.1 In chlorinated water supply systems

Overall, simulated distribution system tests predicted the formation of THMs, HAAs, HANs and HAcAms in both chlorinated systems (WTW A & B) during all sampling rounds. In addition, the tests simulated well the speciation transformation of the DBPs in the distribution networks, which is another main finding.

#### 5.2.1.1 Trihalomethanes (THMs) in chlorinated SDS tests

Indeed, THMs concentrations increased linearly as water age increased and chlorine residual was decreased in the incubation bottles, a trend that was observed during all seasonal sampling rounds at both free chlorinated systems. This trend was consistent with the results obtained from the actual distribution locations and with literature (Koch et al. 1991; Rossman et al. 2001; Rodriguez et al. 2001). **Figure 5.9** and **5.10** demonstrate the results obtained from the SDS tests against those obtained in the actual distribution system for water treatment works A and B, respectively. Total THM concentrations varied between the seasonal sampling rounds, since water temperature is an important factor that inhibited or deterred their formation in the simulated distribution systems. In **water works A**, THMs concentrations after 6 hours (*minimum incubation time*) were the lowest observed, while the highest were identified after 106 hours (*maximum incubation time*), during all four seasonal samplings. The increases in THM concentrations were significant between 6 and 106 hours, ranging from 50.4 to 68.3 %, averaging 59.8% during the four sampling rounds (49.35% average in actual distribution system). The deviation of increase rate between the SDS tests and actual samples is due to the water age uncertainty, given in ranges for actual systems, while SDS tests were quenched in exact intervals. Furthermore, even though the total concentrations presented seasonal dependence, this was not the case with the increase rates, since there was no correlation between water temperature and formation rate. It is noteworthy though that in general the concentrations followed higher increase patterns in lower water ages (between 6 and 24 hours) than in higher water ages (between 48 and 106 hours). This indicated that the THMs were following a rapid generation rate in the early stages of distribution, possibly even immediately after the disinfection step. As mentioned above, THMs formation was influenced by the water temperature in which there were incubated, which was the same as the one measured in situ during the sampling day. The highest THM concentration reported in the SDS tests of WTW A was 75.4 µg/L after 106 hours during Round 4, when samples were incubated at the highest temperature of 22°C. The relative concentration of the actual distribution system in A-L3 after 72-106 hours during the same round was 71.0 µg/L, so there is a statistically minimal deviation between the two identified concentrations. Once more, during the winter sampling round (Round

2), simulated tests presented the lowest total concentrations, ranging from 15.6 to 48 µg/L (20.5 to 42.3 µg/L in actual distribution system). Generally, the concentration of the actual distribution samples would fall between the concentrations of the simulated samples of the exact minimum and maximum hours of each range. This was expected since the water age ranges were produced by modelling whereas the simulated samples were quenched in exact times. However, in several cases, particularly in low water ages (6-12 hours), it was observed that the THM concentrations from the actual distribution locations exceeded those from the SDS tests of 6 and 12 hours. This was possibly related more to the complex hydraulic conditions that enhanced chlorine reactions in the actual network than in the bottles.

In WTW B, THMs concentrations also increased significantly with water age, with the minimum total concentration during each sampling observed in 6 hours and the maximum observed in 106 hours. The increases in THM concentrations were significant between 6 and 106 hours and fluctuated between the sampling rounds, ranging from 59 to 107.2 %, averaging 76.4% during the four sampling rounds (47.7% average in actual distribution system). Contrary to the actual distribution samples, the increased rate in B WTW simulation samples (between 6 and 106 hours) followed a seasonal pattern with considerably elevated increased rate during summer (Round 4 ~ 22°C), medium and similar increased rate during spring and autumn (Round 1 & 3 ~ 17°C & 14°C) and low rate during winter (Round 2 ~ 8°C). This observation is consistent with theoretical expectations concerning the effect of temperature variations on the kinetics of chlorine consumption (Roccaro et al. 2008). However, the fact that it was highlighted from the SDS samples demonstrated the tool's prevalence over results and trends precision. Also, the fact that the actual distribution locations are characterised by water age ranges of several hours it was expected to present more ambiguous trends, especially in THMs that form rapidly in the initial stages of distribution (US Environmental Protection Agency 2010) and thus a chlorinated sample of 6 hours might present considerable concentration differences than that of 12 hours.

Total THM occurrence from SDS samples presented the same seasonal and water age dependency as actual distribution samples, since the maximum yield was reported after 106 hours during Round 4 (71.5 µg/L), when SDS were incubated in the highest test temperature of 22°C, whereas the concentrations are significantly lower when SDS samples were incubated at 8°C, to simulate the water temperature of Round 2 (winter). It is noteworthy, that even though TOC values were similar between the two sampling rounds, total THM concentration after 106 hours during Round 2 (winter) is similar to that of 24 hours during Round 4 (summer). This demonstrated the dominance of several parameters, such as water temperature,

against others with the regards to the formation of trihalomethanes. However, similarly to WTW A it was expected that the concentrations of the SDS tests would form the lower and upper boundaries of the relative actual distribution concentrations. However, in WTW B this was observed only in two sampling rounds (Round 2 & 4), whereas during the other two rounds THM concentrations from the actual distribution locations exceeded those from the SDS tests, not only in low water ages but also in high water ages, something that was not expected. This might be related to underestimation of the water age ranges in the actual distribution network of B WTW, due to the inherent uncertainty in determining water ages by modelling. In fact, even the actual distribution concentrations that were between the boundaries, occurred in close levels with its upper water age boundary of the SDS tests; THM occurrence at 24-48 hours was closer to the occurrence of 48 hours of the SDS samples. If this assumption is wrong, then SDS tests in B WTW slightly underestimated the occurrence of THMs. Yet, the deviation to be expected is of a level of approximately 10%, translated in average of 4.5 µg/L, which is almost an inconsiderable deviation from a water utility standpoint. This percentage was calculated by subtracting the identified level in actual distribution from that of SDS tests, divided by itself and multiplied by 100.

Nevertheless, SDS tests not only simulated the formation of THMs but also the speciation in both chlorinated systems (Koch et al. 1991), the SDS test speciation results also followed the same formation pattern and yields of chloroform and brominated THMs. Similarly, to the relative actual distribution locations, brominated species represented the majority of THM occurrence, with the most predominant species being dibromochloromethane (DBCM). This indicated that the bromide incorporation in the incubation bottles occurred in similar levels as in the actual networks. In fact, in WTW A where bromide levels were always <12 µg/L, chlorine-containing THM (chloroform) presented a median yield of 15% of TTHM (*16% in actual distribution system*), whereas the brominated-containing presented a median yield of 85% of TTHM (*84% in actual distribution system*). In the results of SDS tests in B WTW, where bromide was quantified above 12 µg/L, chlorine-containing THM (chloroform) presented a median yield of 11% of TTHM (*9% in actual distribution system*), whereas the brominated-containing presented a median yield of 89% of TTHM (*91% in actual distribution system*).

#### **5.2.1.2 Haloacetic acids (HAAs) in chlorinated SDS tests**

Furthermore, SDS tests seemed to simulate very well the formation and degradation of HAAs in both chlorinated systems. **Figure 5.11** and **5.12** demonstrate the results obtained from the SDS tests against those obtained in the actual distribution system for water treatment works A and B, respectively. Overall,

it can be noted that the concentrations that are generated during the lowest incubation time (6 hours) are similar or slightly higher with those that occurred in the highest incubation time (106 hours), regardless of the intermediate occurrence variations. In any case, the magnitude of the increase in HAA concentrations during chlorination (median: 9% from 6 to 106 hours) was less than the increase observed for THMs (median: 60%). Indeed, for WTW A the maximum increase reported from 6 to 106 hours was 12%, translated into 4.8 µg/L from the initial to the final distribution location. This was also observed from actual distribution samples, which indicated that water age was not one of the main factors that influenced total HAAs formation in distribution. The results obtained from the actual distribution systems were indicative of the expected trends to be observed concerning the HAAs occurrence in the networks, the SDS on the other hand, were proven to be more descriptive on the intermediate patterns. More specifically, it was observed that the SDS samples from WTW A presented a consistent pattern with regards to individual water ages during all four sampling rounds. Total HAA concentrations presented a slight increase (7% median) from 6 to 12 hours, following a further increase until 24 hours (8.1% median), where they reached a peak. Indeed, maximum HAA concentrations in SDS tests were identified at 24 hours during all sampling rounds in WTW A. After 24 hours, HAA concentrations presented a decrease until 48 hours (18% median), and a subsequent increase until 72 hours (5.2% median). The concentrations observed after 72 hours were either similar or slightly lower than that of 106 hours. The increases are related to continuous oxidation reactions in the presence of chlorine residual, in low water ages, or the accumulative effect of other DBPs decomposition, in higher water ages (Zhang and Minear 2002). It is surprising though that degradation of the HAAs was observed in the SDS samples, since this tendency is mainly related to factors that bottles incubation were unable to simulate, such as interactions with pipe corrosion materials or microbial activities (Tung and Xie 2009). However, the presence of bacterial isolates in the SDS samples cannot be excluded since the water used for incubations was collected prior to disinfection in the water treatment works. Thus, the chances of microbial carry over in the SDS bottles was high and possibly responsible for HAAs biodegradation in the chlorinated systems (McRae et al. 2004; Zhang et al. 2009). The decrease in total HAAs, may also be associated with the hydrolysis of tri-HAA to their corresponding THMs at the pH reported in the bottles (pH range: 7.2-7.9) (Reckhow et al. 1990). If this assumption is not correct, abiotic degradation might have occurred in the SDS samples; hydrolysis or reductive dehalogenation of HAAs (Zhang and Minear 2002; Hozalski et al. 2008) induced with the pH increases observed in two rounds after 24 hours. In WTW B, the HAA results from SDS samples presented formation and decay trends that were

seasonally dependent, meaning that HAAs presented different behaviour in each incubation temperature. In more detail, when SDS tests were incubated at the maximum test temperature (22°C), average total HAA concentrations were consistently increasing between 6 and 48 hours (36% *median*), with a subsequent decrease at 72 and 106 hours (16% *median*). When SDS tests were incubated at the minimum test temperature (8°C), average total HAA concentrations increased until 24 hours (16% *median*), then followed a minimal decrease until 48 hours and finally levels increased back again until 106 hours. On the other hand, SDS tests that were incubated in medium temperatures (17&14°C), followed an early decrease at 24 hours (22% *median*) with a consistent subsequent increase until 106 hours (25% *median*). Even though the formation and decay pattern observed in WTW B was complicated, it indicated that overall total HAAs levels slightly increased between 6 and 106 hours, ranging on average 15-25%, translated into 2- 9.3 µg/L. In practice, the above findings concerning the formation/ decay patterns of HAAs in simulated distribution systems suggested that the implementation of this tool by water utilities will give a good estimation of the occurrence levels to be expected at the final location the system within 6 hours, whereas the maximum concentrations could be identified between 24 and 48 hours. Furthermore, the formation of total HAAs in SDS samples had a strong correlation with water temperature, since significantly lower concentrations were reported when the chlorinated samples were incubated at 8°C, to represent Round 2 (winter) in comparison with those reported in all the rest incubation temperatures. It is interesting, that in WTW A the median total HAA levels were approximately 80%, 71% and 78% greater in summer (22°C), autumn (17°C) and spring(14°C), respectively, than this of winter. These percentages between seasonal sampling are consistent will previous HAAs studies occurrence in the UK (Graham et al. 2009) but not as momentous as these reported in a Canadian study (Rodriguez et al. 2004); that saw four fold lower concentrations during winter. The SDS tests apart from simulating the spatial and temporal variation of HAAs occurrence in the chlorinated systems, they also captured the speciation of the HAAs generated. Concerning the HAAs speciation, the dominant HAA species was dichloroacetic acid (DCAA), followed by dibromoacetic acid (DBAA), the same previously reported to occur in the selected actual distribution locations. In general, the weight ratios of bromine containing HAAs species identified were higher than that of the chlorinated ones, averaging 60% (58% *in actual downstream locations*) and 55% (57% *in actual downstream locations*) in WTW A and WTW B, respectively. In addition, SDS results indicated that di-haloacetic acids were more prominent than tri-haloacetic acids in both chlorinated systems (Weinberg et al. 2002), except during the incubation with the lowest water temperature (*Round 2-winter*). Previous literature had observed that

during chlorination TXAA species may be higher than DXAA (Cowman and Singer 1996; Baribeau et al. 2006; Zhang et al. 2009; Graham et al. 2009), however this was not observed in this study. Weinberg et al. (2002) had previously linked the dominance of dihalogenated HAAs in the ability of *pre-ozonation* in removing more efficiently tri-HAA precursors during water treatment (di-HAAs precursors are more hydrophilic than tri-HAAs); pre-ozonation was applied in both selected chlorination systems of this study and therefore explains the dominance of di-HAA. The dominance of tri-HAAs, only during low temperature incubation, was not due to environmental conditions that influenced any increase, but was mainly due to decrease of the DXAA ones that represented the major fraction of total HAAs.

Also, the results indicate that the weight ratios of regulated (HAA<sub>5</sub>) to total HAAs were similar in both free chlorinated systems investigated, averaging 61% (67% *in actual downstream locations*) and 69% (68% *in actual downstream locations*), for WTW A and B, respectively. These results suggested once more that the non-regulated HAAs comprise a significant proportion of the HAAs in the selected systems, even though the bromide levels are relatively low. Generally, the HAA<sub>5</sub> to total HAAs weight ratios followed the same formation and decay pattern as the total HAAs levels in the two systems, since the representative species of HAA<sub>5</sub> are the ones more susceptible to degradation (Baribeau et al. 2006).

The results obtained from the simulation of the distribution networks indicated that both THMs and HAAs concentrations were similar as in the actual distribution systems, and even followed the same formation/decay trends with regards to water age. The deviations observed were considered statistically minimal and therefore are not important from a practical standpoint. Furthermore, SDS tests also simulated the speciation of THMs and HAAs within the selected chlorinated distribution systems. The accurate prediction of the above DBP classes, already known to be predicted by SDS tests, validated the performance of the SDS tests performed in our lab. Therefore, the same tests were applied to investigate their potential in predicting the occurrence and speciation of nitrogenous DBPs; HANs and HAcAms.

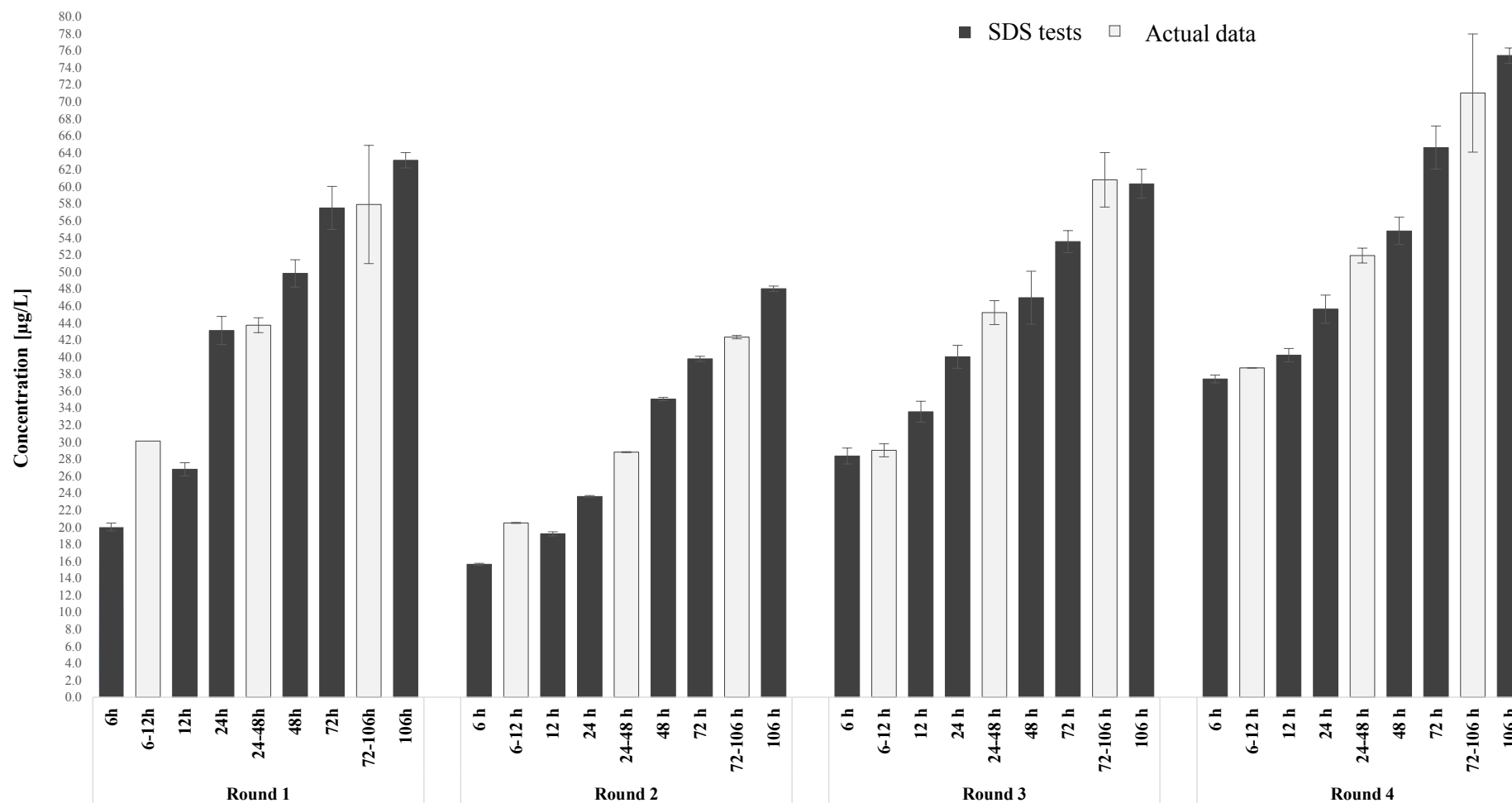


**Figure 5.9:** Total THMs (chloroform, BDCM, DBCM, bromoform) occurrence in SDS tests and actual distribution from chlorinated **WTW A**.

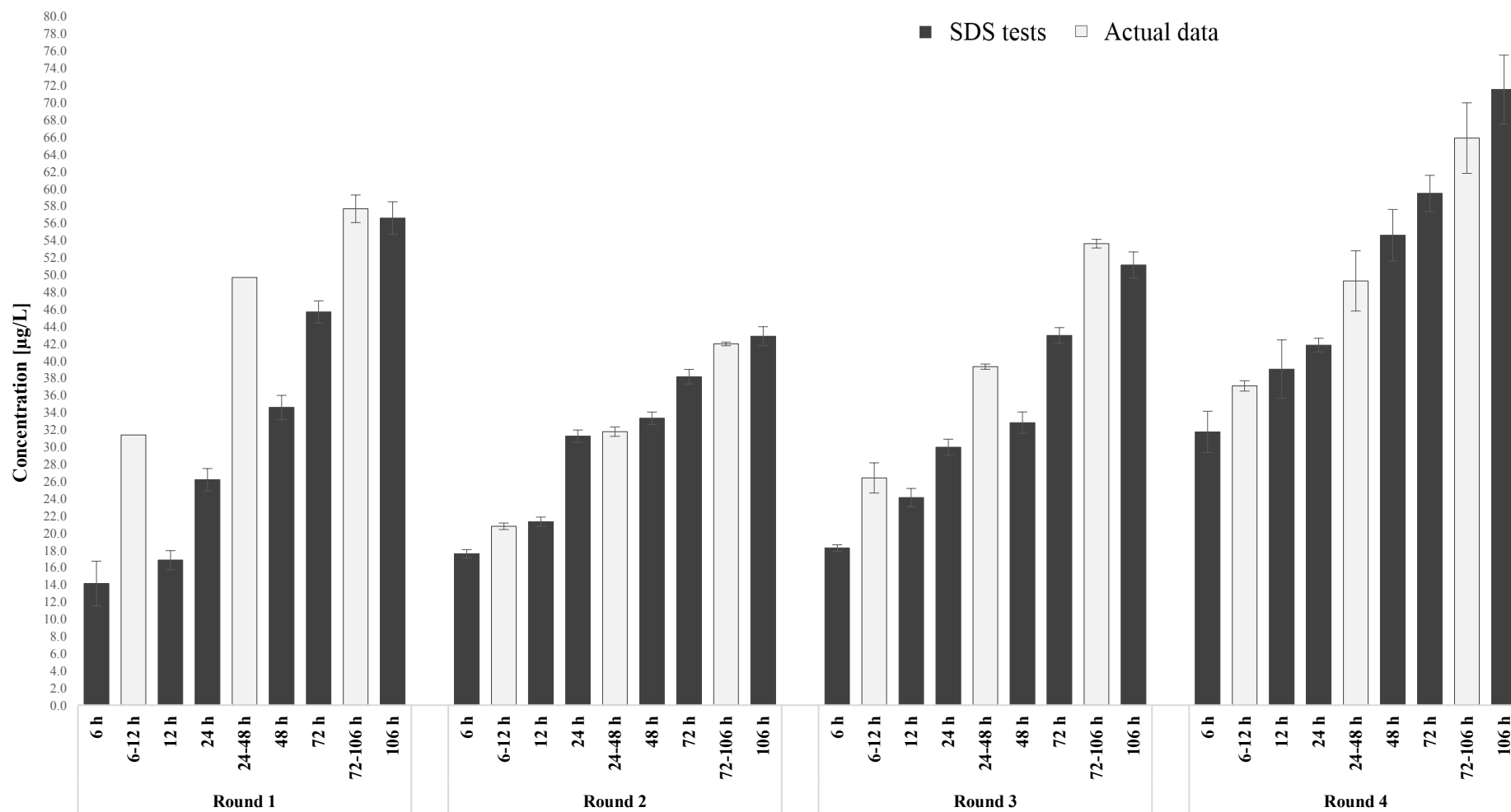


**Figure 5.10:** Total THMs (chloroform, BDCM, DBCM, bromoform) occurrence in SDS tests and actual distribution from chlorinated **WTW B**.

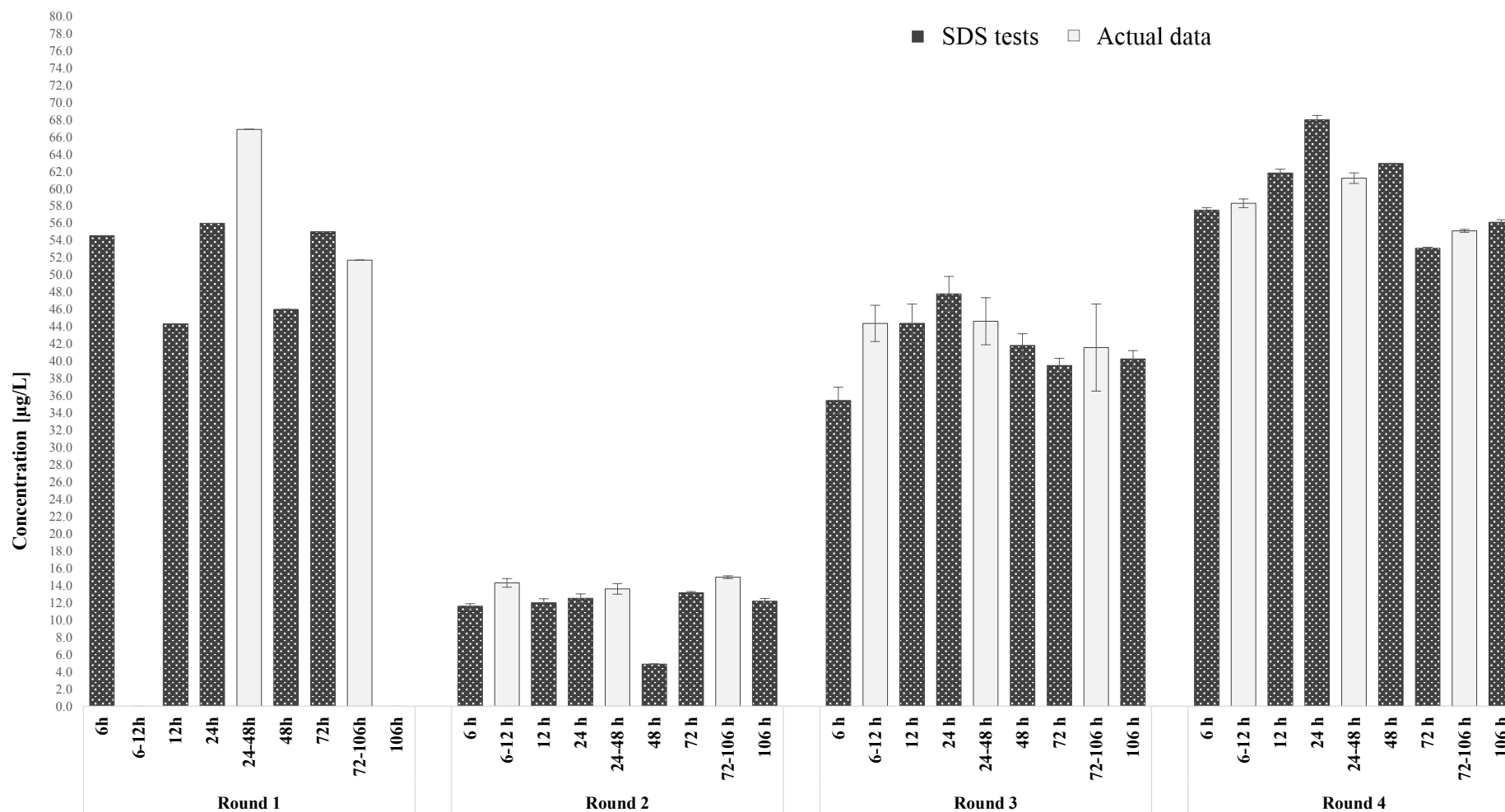


**Figure 5.11:** Total HAAs (MCAA, MBAA, DCAA, TCAA, DBAA, BCAA, BDCAA, DBCAA, TBAA) occurrence in SDS tests and actual distribution from chlorinated **WTW A**.

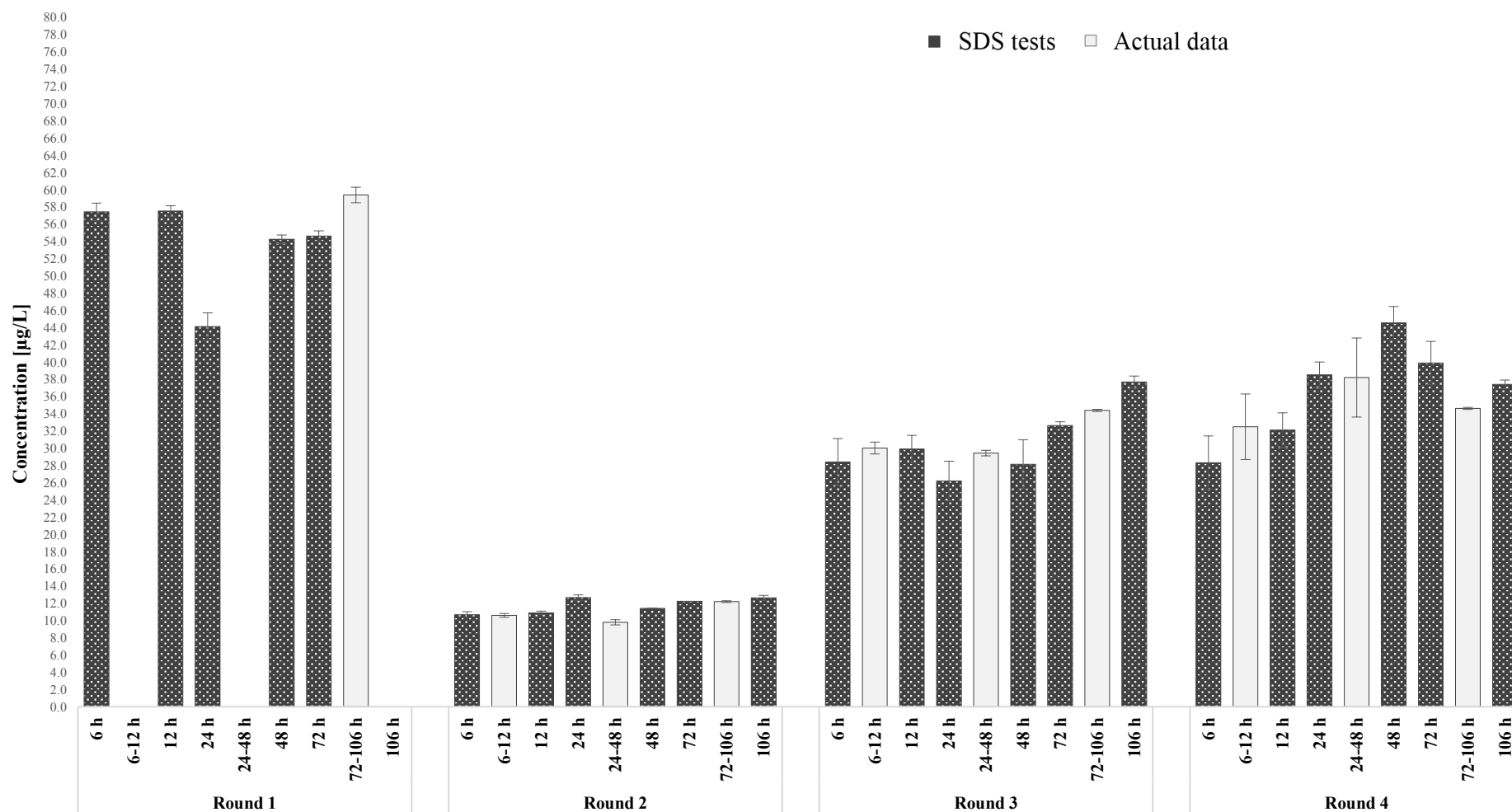


**Figure 5.12:** Total HAAs (MCAA, MBAA, DCAA, TCAA, DBAA, BCAA, BDCAA, DBCAA, TBAA) occurrence in SDS tests and actual distribution from chlorinated **WTW B**.

### 5.2.1.3 Haloacetonitriles (HANs) in chlorinated SDS tests

The SDS test effectively estimated the formation and degradation of both target N-DBP classes, HANs and HAcAms in the selected chlorinated systems. The levels of HANs and HAcAms reported from the SDS were statistically similar with those quantified in the actual distribution samples during all sampling rounds. Once more, from the seven selected HANs, only five of them were identified, whereas from the nine HAcAms, eight were identified with the analytical methods applied. The total HAN concentrations reported by the SDS tests were  $<9 \mu\text{g/L}$  with a median value of  $3.9 \mu\text{g/L}$  and  $3.8 \mu\text{g/L}$ , in A and B WTW, respectively. **Figures 5.13** and **5.14** show the fate of HANs levels in the simulated distribution system tests in comparison with those reported from the actual distribution locations as a function of the water age. These figures demonstrate that most of total HAN concentrations identified in actual systems are found to be between the concentrations identified in the lower and upper limits of their water age ranges, expressed as incubation times in SDS tests. However, some exceptions are observed especially in low water ages, where the HANs levels in SDS were slightly lower than those identified in the actual networks during the same water ages. Other determining factors, such as pH and chlorine residual, were not statistically different between the actual and simulated samples, to explain the deviation. This underestimation is possibly due to low circulation and mixing conditions in the SDS bottles that may have limited or detained reactions between the NOM and chlorine at these water ages. The deviation between the SDS and real distribution values was minimal from a practical viewpoint, with the largest difference being  $2.1 \mu\text{g/L}$ . The above observation was neither confirmed nor contradicted by Koch et al. (1991), where HAN levels between the two set of samples did not present a pattern.

Generally, it was reported that HANs concentrations increased between the lowest (*6 hours*) and the highest incubation time (*106 hours*), in both chlorinated SDS samples, with varying increase rates; either less than 2% or more than 60%. This has been previously reported by Bond et al. (2015) and Weinberg et al. (2002), in nationwide occurrence studies where HANs levels presented a slight increase within the initial and final location of real and simulated distribution networks. Apart from the overall increases, decays were also observed in intermediate incubation times. However, these decays were not that significant to reset the total HAN concentrations to their minimum levels, which were reported only in 6 hours during all four sampling rounds. Moreover, it is not safe to say that a formation/degradation pattern is observed in the chlorinated systems between the sampling rounds. Nevertheless, the median values from the SDS tests indicated that total HANs increased until 24 hours and then slightly decreased until 48 hours. Following that, HAN levels

increased again in the samples incubated at 72 and 106 hours. The decrease observed around 48 hours is related to HANs hydrolysis to form their HAcAms counterparts. The first study by Koch et al. (1991) in chlorinated SDS tests also reported that HAN levels increased until 24 hours, decreased until 72 hours and then increased back again to be very similar to the initial concentrations of 3 hours.

Also, HANs occurrence was not characterised by any seasonal variability, since similar levels were identified in low and high water temperature incubations. This observation suggested that the HANs generations was mainly affected by the constituents of the water matrix, rather than the environmental conditions, during each sampling round.

Furthermore, SDS tests also predicted the speciation of HANs in the distribution networks. The presence of relatively low bromide impacted the speciation by promoting the formation of brominated species. Similar to what was observed in actual distribution samples, the most predominant HANs species in SDS tests were DBAN, followed by BCAN. During the majority of the sampling rounds the brominated species ranged between 60-100% and 72-100%, in WTW A and B water samples, respectively. An exception was observed, though, during round 4 (*summer*) especially during low water ages, which was confirmed by the findings of actual distribution samples; chlorine-containing species, and particularly TCAN, were more abundant, representing a median weight fraction of 67%. This was possibly due to the increased chlorine demand during that period because of the reported algae outbreak and the high water temperatures (Knappe et al. 2004), that shifted the chlorine to bromine ratio in the water samples.

#### **5.2.1.4 Haloacetamides (HAcAms) in chlorinated SDS tests**

A key question posed during this study was whether HAcAms formation and speciation can be predicted via the implementation of simulated distribution systems. It is already known that SDS tests have been successfully implemented to predict the occurrence of THMs, HAAs and 3 species of HANs (Koch et al. 1991). Therefore, the direct comparison of our findings between the actual distribution samples and the SDS samples for the above three DBP classes enabled the validation of the SDS tests performance in our water samples and encouraged the assessment of the tests concerning the HAcAms occurrence. The concentration of total HAcAms produced in the chlorinated distribution locations of WTW A and B was compared to that reported in the incubation bottles in all selected water ages, during all four sampling rounds. These results are summarised in **Figure 5.15** and **5.16**, which illustrate that the predicted and actual total HAcAms levels as a function of water ages, in the chlorinated A and B WTW systems, respectively. From these graphs, it was initially observed that there was a repetitive trend for more HAcAms to be

produced in actual distribution networks than in SDS tests over the same amount of time. This was mainly observed in the samples that represented medium to high water ages (24-106 hours), due of the competing and complex formation and degradation reactions that occurred at this stage of distribution (AWWA 2002). In addition, the presence of reservoirs of organic materials either in the scale, tubercles, or biofilm attached to the pipe walls, that may have acted as supplementary HAcAm precursors, was possibly more elevated in locations of high water ages. The deviations between the two sets of samples ranged between 0.1-2.6  $\mu\text{g/L}$ , averaging 1.2  $\mu\text{g/L}$ , therefore SDS tests predicted, even conservatively, the total HAcAms levels to be expected in the given water ages. From the data obtained, total HAcAm concentrations in SDS samples were always  $< 10 \mu\text{g/L}$  in both chlorinated systems, with median values of 3.6  $\mu\text{g/L}$  (3.4  $\mu\text{g/L}$  in *actual distribution samples*) and 3.5  $\mu\text{g/L}$  (4.0  $\mu\text{g/L}$  in *actual distribution samples*), in A and B WTW, respectively. Unfortunately, there was no consistent relationship between the occurrence of HAcAms or the magnitude of intermediate increases and decays, and water age in both chlorinated systems. However, the intermediate fluctuations observed in SDS tests agreed with those that occurred in actual distribution systems. More specifically, in SDS samples of WTW A, HAcAms were observed to both increase and decrease between 6 and 106 hours, whereas were observed to slightly decrease in SDS samples of B WTW. In more detail, median HAcAm concentrations in WTW A indicated an increase between 6 and 12 hours, followed by a decrease between 12 and 24 hours. This degradation was always occurring around 24 hours, which was due to HAcAm hydrolysis and subsequent formation of the relative HAAs, confirmed from HAAs levels in the same incubation time during all sampling rounds. Then, median concentrations after 48 hours would either follow an increase, partially related to HANs hydrolysis, or would continue to degrade until 106 hours. Likewise, in SDS samples of WTW B, HAcAms followed an increase rate until 12 hours in three of the four sampling rounds, and then either increased or decreased by various generation/decay rates. In the SDS samples of WTW B, the HAcAm increases are not coincided with the hydrolysis of HANs that indicated the independent formation of HAcAms from separate precursors. These different patterns within the same system during the various sampling rounds was not influenced by water temperature, or any other measured water quality parameter (e.g. pH, TOC), but was more related to the nature of the organic precursors of the water matrix.

Even though this was not the focus of this research, other studies have indicated that NOM quality is characterised by seasonal variations (Sharp et al. 2006; Teixeira and Nunes 2011) in terms of molecular weight, solubility and functional group composition. Interestingly, one of the most reactive fractions of

NOM, the fulvic acid fraction has been reported to double between autumn and winter (Sharp et al. 2006). The SUVA values calculated gave limited information on the changing character of WTW A and B water over the annual sampling, and possibly fluorescence analysis would have been more informative. Another point of interest in this study was the prediction of the HAcAms speciation via the implementation of SDS tests. When the actual distribution results were compared with those identified in the incubation bottles, the weight ratios of bromine containing HAcAms species were very similar, averaging 68% (*64% in actual distribution*) and 61% (*55% in actual distribution*) during the various incubation times, in A and B WTW SDS samples, respectively. It is surprising that even though water samples from WTW B presented slightly higher concentrations of bromide ions than WTW A, the percentile generation of brominated species was more abundant in A WTW SDS samples. This highlighted that significant amounts of brominated HAcAms species were generated even in waters with relatively low bromide concentration, therefore the incorporation of bromide ion was very elevated in the case of HAcAms. Similarly to actual distribution systems, the most dominant HAcAm species in both chlorinated SDS samples was BCACAm, followed by TCACAm and DCACAm.

Overall, it was observed that SDS test results encompassed the ranges of HANs and HAcAms concentrations and speciation expected to be identified during the different water ages within the chlorinated distribution systems. Total HAN concentrations that were predicted to generate in the early stages of distribution are similar or slightly higher (*by 0.1-4.3 µg/L*) at the final stages, regardless of the intermediate increases and decreases. Total HAcAm concentrations that were predicted to generate in distribution did not present any significant temporal pattern, since both total HAcAms increases and decreases occurred between low and high incubation times.

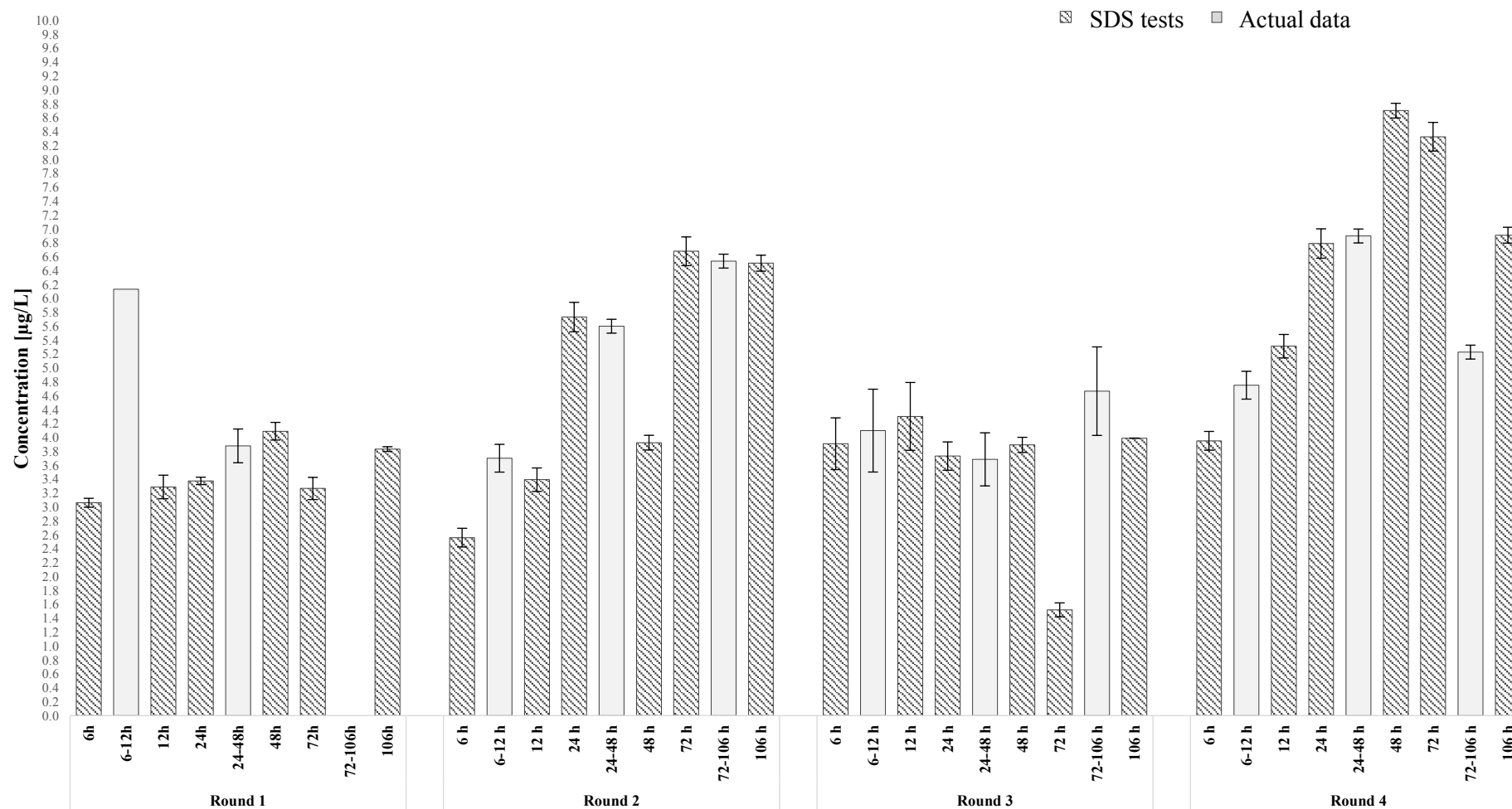


**Figure 5.13:** Total HANs (MCAN, MBAN, DCAN, TCAN, DBAN, BCAN, BDCAN, DBCAN, TBAN) occurrence in SDS tests and actual distribution from chlorinated **WTW A**.

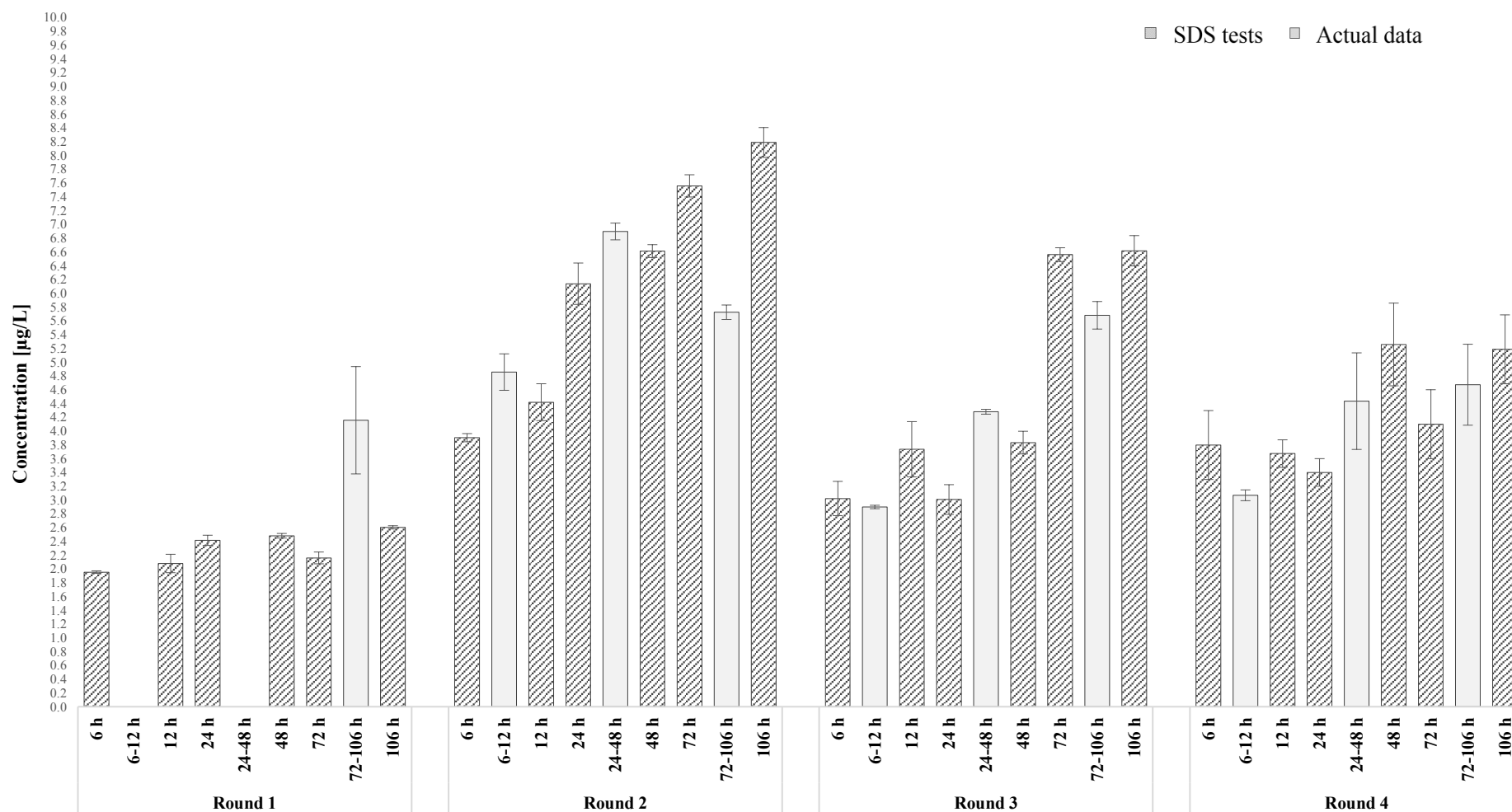


**Figure 5.14:** Total HANs (MCAN, MBAN, DCAN, TCAN, DBAN, BCAN, BDCAN, DBCAN, TBAN) occurrence in SDS tests and actual distribution from chlorinated **WTW B**.

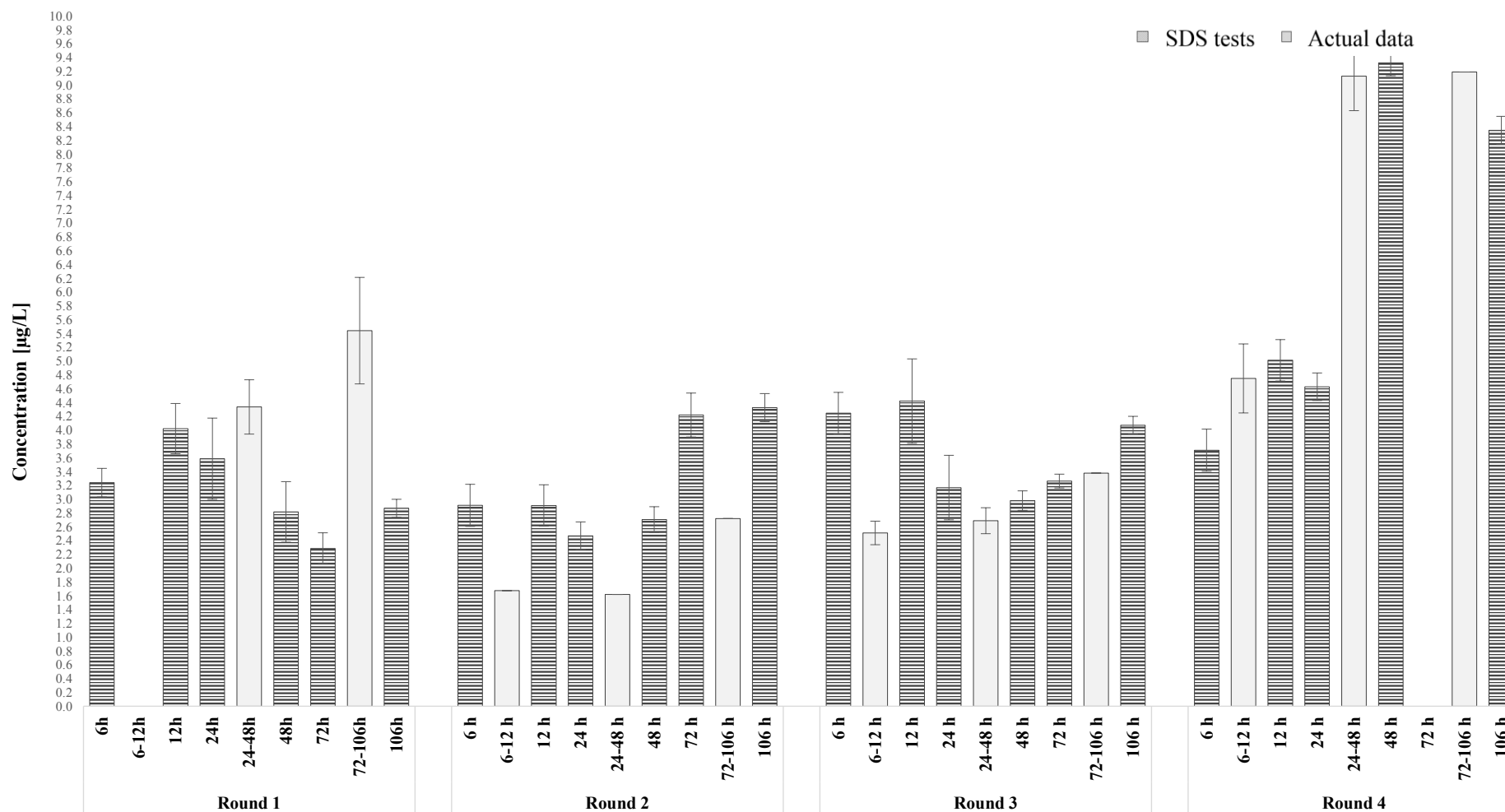


**Figure 5.15:** Total HAcAms (MCaAm, MBaAm, DCaAm, TCaAm, DBaAm, BCaAm, BDCaAm, DBCaAm, TBaAm) occurrence in SDS tests and actual distribution from chlorinated A WTW.

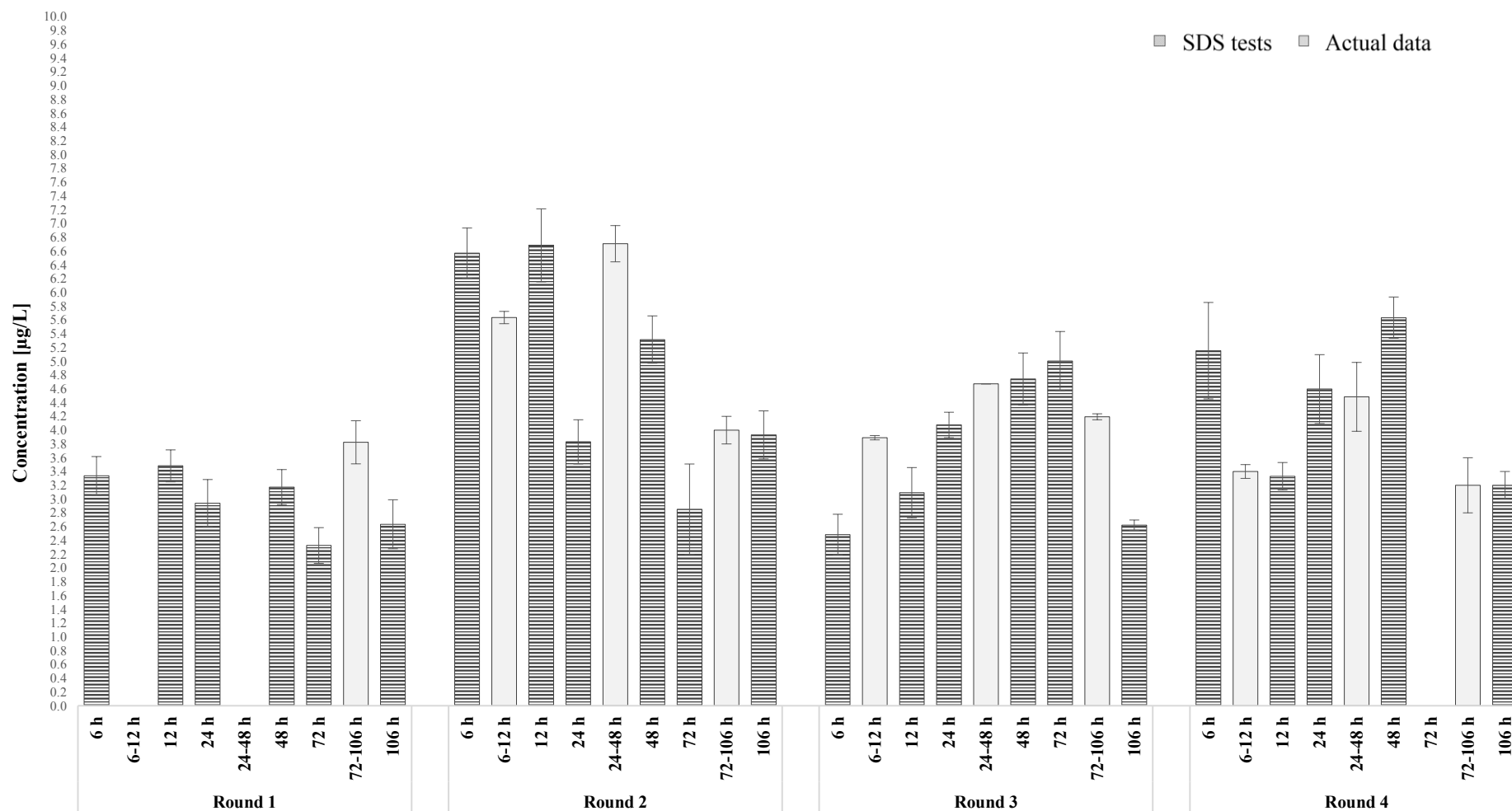


**Figure 5.16:** Total HACams (MCAcAm, MBAcAm, DCAcAm, TCAcAm, DBAcAm, BCACAm, BDCAcAm, DBCAcAm, TBACAm) occurrence in SDS tests and actual distribution from chlorinated B WTW.

### 5.2.2 In chloraminated water supply systems

Chloraminated simulated distribution system tests were also implemented to investigate the potential of this tool to predict the fate and occurrence of THMs, HAAs, HANs and HAcAms in chloraminated distribution systems. The main difference from all the other chloramination experiments of this project was that water samples for the chloraminated SDS tests were not spiked in the laboratory with preformed monochloramine solution but were collected after the disinfection step in the treatment work, taking into account the prior contact time with the disinfectant for the subsequent incubation. This approach was primarily selected to simulate the chloramination practice currently followed by water utilities and thus eliminate the errors between the two sets of data (*actual and simulated*) due to the disinfection mode difference. Besides, the SDS methodology suggests that water collection after disinfection is also an acceptable approach to simulate the formation of DBPs.

Generally, simulated distribution system tests predicted the formation of THMs, HAAs, HANs and HAcAms in both chloraminated systems (WTW C & D) during all sampling rounds. Another important finding as that SDS tests also simulated the speciation of DBPs in chloraminated distribution networks.

#### 5.2.2.1 Trihalomethanes (THMs) in chloraminated SDS tests

THMs concentrations increased linearly as water age increased and chlorine residual was decreased in the incubation bottles, a trend that was observed during all seasonal sampling rounds at both chloraminated simulated systems. This trend was consistent with the results obtained from the actual distribution locations and with literature (Koch et al. 1991; Rossman et al. 2001; Rodriguez et al. 2001). **Figure 5.17** and **5.18** demonstrate the results obtained from the SDS tests against those obtained in the actual distribution system for water treatment works C and D, respectively, as a function of water ages. Total THM concentrations varied between the seasonal sampling rounds, even though not as much as in the chlorinated SDS samples, and presented the same seasonal and temporal dependency as their relative actual distribution samples. In the chloraminated systems THMs were always <40 µg/L even in the highest incubation time, where concentrations are expected to be found in their highest values, and never exceeded the internal limits. Generally, it was expected that the DBP concentrations from actual distribution samples would fall into the extremities of those identified by the relative SDS tests (representative of specific water ages). However, in several cases, particularly in medium water ages (24-48 hours), it was observed that the THM concentrations from the actual distribution locations exceeded those from the SDS tests of 24 and 48 hours

in both WTW C and D. The same was reported to occur in chlorinated SDS tests but in earlier incubation times, which highlighted once more the increased reactivity rate of chlorine against chloramines (Kirmeyer et al. 2000). This underestimation was possibly related to the different hydraulic conditions that occurred in the actual water pipes, however this deviation was never  $> 8.5\%$ , namely was always less than  $2.5 \mu\text{g/L}$ .

In **water works C**, THMs concentrations after 6 hours (*minimum incubation time*) were the lowest observed, while the highest were identified after 106 hours (*maximum incubation time*), during all four seasonal samplings (**Figure 5.17**). The increases in THM concentrations were noteworthy between 6 and 106 hours, ranging from 47 to 56%, averaging 52% during the four sampling rounds (*51% average in actual distribution system*). The deviation of increase rate between the SDS tests and actual samples was statistically minimal and was due to the water age uncertainty that characterised the actual distribution samples. Furthermore, the trends in THM concentrations (increase rates, total levels) were not varying considerably from one sampling event to another. It appears that that these statistically similar trends with water temperature variations are related with the combining effect of chloramines reactivity, the differences in treated water quality or/and type of treatment (Singer et al. 2002). It is noteworthy though that, unlike chlorinated samples, the concentrations followed higher increase patterns in higher water ages (between 48 and 106 hours) than in lower water ages (between 6 and 24 hours). This is possibly related to the fact that chloramines are weaker oxidants than free chlorine and therefore initially promote substitution reactions and then oxidation reactions, with increasing THM formation rates as water age progressed (Baribeau et al. 2006). As mentioned previously water age was a strong indicator of THM formation in chloraminated SDS tests, contrary to water temperature, and therefore the highest THM levels were reported at 106 hours to be  $38.2 \mu\text{g/L}$  during Round 3, when samples were incubated at a medium temperature of  $14^\circ\text{C}$ . Also, the lowest levels were reported at 6 hours during Round 2 (winter) to be  $16.9 \mu\text{g/L}$ , when SDS samples were incubated at the lowest experimental temperature of  $8^\circ\text{C}$ .

In **WTW D**, THM concentrations also increased with regards to water age (**Figure 5.18**), which was expected both from the results of the distribution samples and literature. It was surprising, though, the fact that in one occasion (Round 1  $\sim 17^\circ\text{C}$ ), a decrease in total concentration was observed at the incubation time of 72 hours when total chlorine residual was  $< 0.5 \text{ mg/L Cl}_2$ . This decrease between the SDS samples of 48 hours, that presented the maximum total THM levels, and the incubation time of 72 hours was of approximately 23% and was essentially due to decrease of the THM species that contained chlorine molecules. This has been previously observed in a simulated distribution survey in the US by Baribeau et al. (2006), where anoxic conditions were found responsible

for this incident (Singer et al. 1993), a possible condition in incubation bottles at high water ages. Also, THM biodegradation may occur from the combining effect of nitrifying bacteria and disinfectant decrease (Wahman et al. 2006). Even though microbial identification was not conducted during this study, it was possible that nitrifying bacteria may have degraded THMs. The increases in THM concentrations were important between 6 and 106 hours and fluctuated between the sampling rounds, ranging from 37-67%, averaging 47% during the four sampling rounds (*median: 42% in actual distribution system*).

Furthermore, SDS tests predicted the expected speciation of THMs in both chloraminated systems previously determined by the actual distribution samples of WTW C and D (Krasner et al. 2011). Results from the SDS samples of WTW C indicated that THM occurrence was characterised mainly by brominated THM species (i.e. DBCM and BDCM), whereas SDS samples of WTW D were dominated by BDCM and chloroform. Treated water bromide concentrations in WTW C were relatively high (*median: 82 µg/L*), approximately four times higher than in D WTW, thus it was expected that the weight fraction of brominated species would be significantly higher than that of chloroform. Indeed, in WTW C the bromide-containing species constituted the 82-94% of the total THMs levels during all incubation times (*76.2-94.0% in actual distribution network*). On the other hand, in WTW D the weight fraction ratio of chloroform and bromide-containing was very similar (48:52), as bromide incorporation was reduced due to relatively low bromide levels. The data agreement between the SDS tests and actual distribution samples indicated that the bromide content of water behaved similarly in the incubation bottles levels and the distribution networks. It is noteworthy, that in WTW D the fluctuation of bromide levels was more prominent during each sampling round, the amount of brominated THM species and thus total THM levels was analogous with the bromide levels, which was consistent with observations of previous studies (Luong et al. 1982; Krasner et al. 1989; Hu et al. 2010; Zhang et al. 2010). More specifically, the maximum weight fraction of bromine-containing THMs (*median: 72%*) was reported during the sampling round characterised by the highest bromide levels of 26.4 µg/L, whilst the lowest (*median: 42%*) was reported when bromide levels were the lowest (<12 µg/L). Contrary to other distribution surveys, one of the main findings of this study is that even relatively low bromide concentrations promote the formation of brominated THM species (*and other DBP classes*) and therefore were responsible for higher total THM levels. Finally, the weight fraction of chloroform was slightly increased with increasing water age, with a subsequent decrease of brominated THM species during all sampling events (Baribeau et al. 2006).

### 5.2.2.2 Haloacetic acids (HAAs) in chloraminated SDS tests

Furthermore, SDS tests simulated to a great extent the formation and degradation of HAAs in both chloraminated systems. **Figure 5.19** and **Figure 5.20** demonstrate the results obtained from the SDS tests against those obtained in the actual distribution system as a function of water age, for water treatment works C and D, respectively.

Similarly, to the actual chloraminated systems, SDS samples of WTW C and D followed an overall decrease trend from the lowest incubation time (6 hours) to the highest incubation time (106 hours), regardless of the intermediate fluctuations. These findings were consistent with the data obtained from the relative actual chloraminated distribution results and previous studies (Singer et al. 2002; Bayless and Andrews 2008; Goslan et al. 2009; Parsons and Goslan 2009). When these decreases occurred, they varied from 26-38% in WTW C samples, and from 3-79% in WTW D samples between 6 and 106 hours. The decrease rates in WTW C were narrower and more comparable between the sampling events, whereas in WTW D were wider and fluctuating between the sampling events. These differences were likely to stem from differences in raw water characteristics in combination with the water treatment practices between the two chloraminated treatment works, rather than from the effect of chloramines or water temperature between the sampling events. Yet, in two of the four sampling events (Round 3~14°C and 4~22°C) of SDS tests in WTW C, HAAs slightly increased between 6 and 106 hours (*similar trend in actual distribution*). This is inconsistent with studies that suggest more pronounced HAAs degradation in chloraminated systems of high temperatures (Bougéard et al. 2010), unless this was counterbalanced in our system by high disinfectant residuals and high SUVA (*approx. 2.8*). Furthermore, as in the chlorinated SDS tests, it was surprising that HAAs degraded in the SDS bottles of chloraminated systems, and to a level that accurately represented the degradation occurring in the actual distribution samples, since incubation bottles were unable to simulate interactions with pipe corrosion materials or microbial activities (Tung and Xie 2009). However, the samples were not sterile, as later identified in the lab by microbiological analysis, thus the chance of biological activity in the chloraminated SDS bottles was high and possibly responsible for HAAs biodegradation (McRae et al. 2004; Zhang et al. 2009). Indeed, the decreases in HAA levels were generally associated with losses in mono- and di-HAAs, the most biodegradable species (Williams et al. 1997; Zhou and Xie 2002), while tri-HAAs remained relatively preserved in most of the sampling rounds. However, in WTW D during Round 1 (autumn ~ 17°C), tri-HAAs followed a significant decrease after 24 hours in all of the subsequent water age samples until 106 hours. Under the experimental conditions, where there was

no irradiation or heating, the behaviour of tri-HAA species was unable to be explained with the current literature, even though volatilisation has been previously proposed (Chen and Weisel 1998).

An interesting point was that unlike chlorinated water samples, the occurrence of HAAs in both chloraminated systems had poor seasonal dependency, which was confirmed by the statistical correlations. Even though, the total HAAs were generally lower (approx. 31% in C and 47% in D) in cold water temperature (*Round 2~8°C*) than those during the highest water temperature (*Round 4~22°C*) in the various water ages, the HAAs results during the intermediate sampling rounds that presented medium water temperatures were not characterised by a trend. It was therefore likely that water temperature in chloraminated systems was not important enough to determine HAA levels, and that other factors such as pH, HAcAms hydrolysis or NOM nature (Baribeau et al. 2006) were more crucial.

When the occurrence of HAAs from SDS tests and actual distribution samples were compared, it was generally expected that the DBP concentrations from actual distribution samples would fall into the extremities of those identified by the relative SDS tests (representative of specific water ages). However, in the few cases in which there was a deviation between the two set of samples, it was observed that SDS tests slightly overestimated HAAs levels (*max deviation: 7.5% → 1.9 µg/L*) in low water ages (6-24 hours) and slightly underestimated HAAs levels (*max deviation: 40% → 15 µg/L*) in high water ages (72-106 hours). Both the two instances may be related to the inability of SDS to mimic the exact mixing and hydraulic conditions of the water pipes and therefore may delay the formation or decay of HAAs.

The SDS tests apart from simulating the spatial and temporal variation of HAAs occurrence in the chloraminated systems, also captured the speciation of the HAAs. As in actual chloraminated distribution systems, the dominant HAA species were tribromoacetic acid (TBAA), dibromoacetic acid (DBAA) and dichloroacetic acid (DCAA). In general, the weight ratios of bromine containing HAAs species identified were significantly higher than that of the chlorinated ones, averaging 62% (60% *in actual downstream locations*) and 59% (57% *in actual downstream locations*) in WTW C and WTW D, respectively. Di-HAAs and Tri-HAAs accounted for the majority of HAA levels, with di-HAAs being the most prominent species in both chloraminated systems, which was confirmed by previous studies concerning HAAs speciation in distribution during chloramination (Cowman and Singer 1996; Weinberg et al. 2002; Philip C. Singer et al. 2002). Also, the SDS results predicted with precision the weight ratios of regulated (HAA<sub>5</sub>) to total HAAs which were similar in both chloraminated systems selected, averaging 28% (33% *in actual downstream locations*) and 40% (40% *in actual downstream locations*), for C and D WTW, respectively. Greater

bromide concentrations, as in C WTW, lead to even lower HAA<sub>5</sub>-to-HAA<sub>9</sub> mass ratios as the bromine-containing species are not adequately represented by HAA<sub>5</sub>. These results highlighted that the identification of the five regulated HAAs is only representative of one third of the total HAA levels occurring in chloraminated distribution systems, and therefore provides limited information of seasonal and temporal patterns for the design of operational strategies. Moreover, in chloraminated SDS tests similarly to chlorinated, the HAA<sub>5</sub>-to-HAA<sub>9</sub> mass ratios either remained stable or followed the same formation and decay pattern with increasing water age. This was an anticipated pattern as the HAAs species more susceptible to biodegradation, such as mono- and di-haloacetic acid species are the representative species of HAA<sub>5</sub> (Williams et al. 1997).

From a practical standpoint, the implementation of SDS tests by water utilities will provide a useful insight on the expected HAA levels and speciation in chloraminated systems if followed in precision to capture all intermediate fluctuations, since contrary to THMs the prediction of HAAs was more site and temporal specific.

The accurate prediction of the above DBP classes, already known to be predicted by SDS tests, validated the performance of the SDS tests performed in our lab. Therefore, the same tests were applied to investigate their potential in predicting the occurrence and speciation of nitrogenous DBPs in chloraminated systems; HANs and HAcAms.

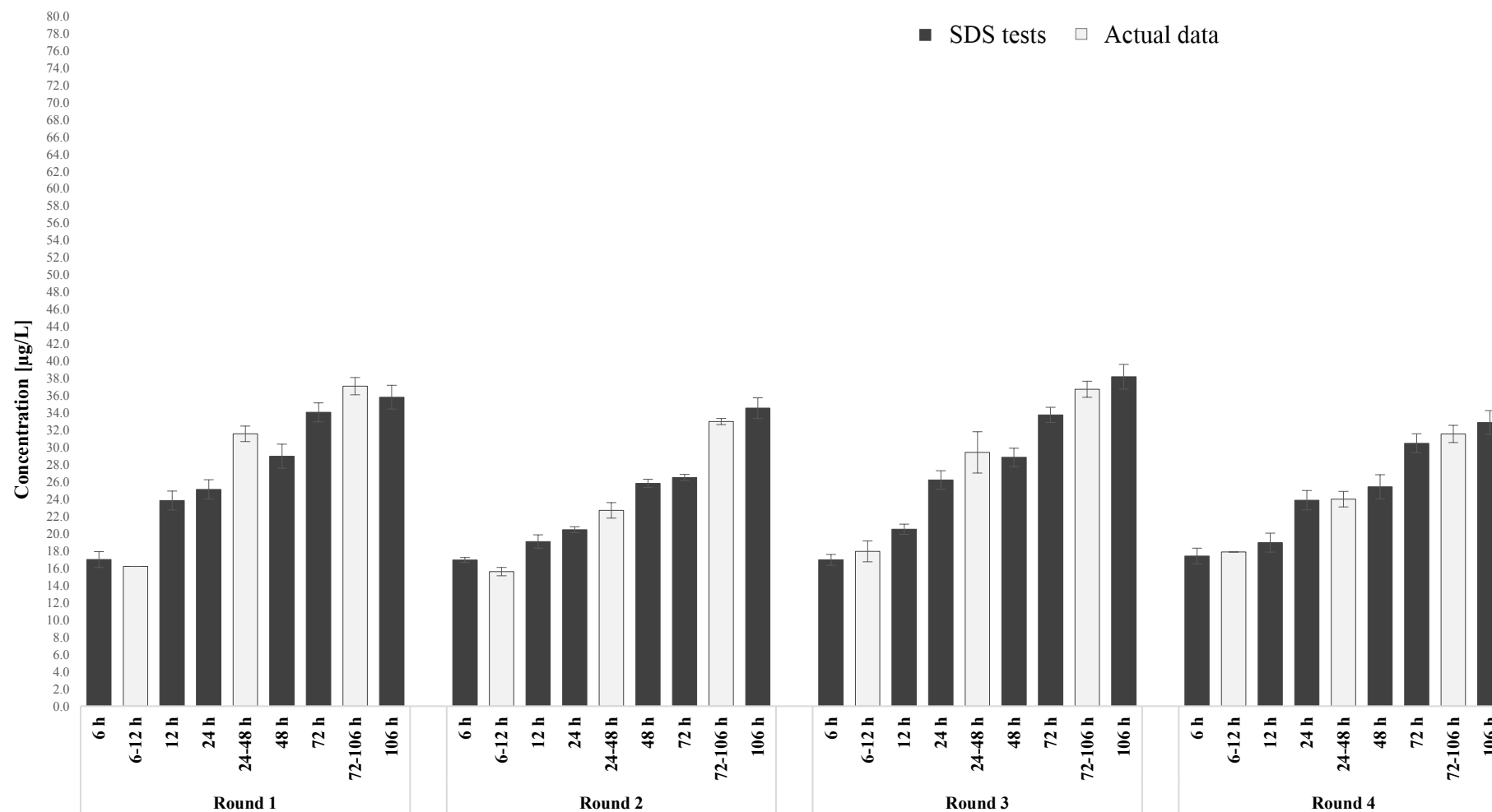


**Figure 5.17:** Total THMs (chloroform, BDCM, DBCM, bromoform) occurrence in SDS tests and actual distribution from chloraminated WTW C.

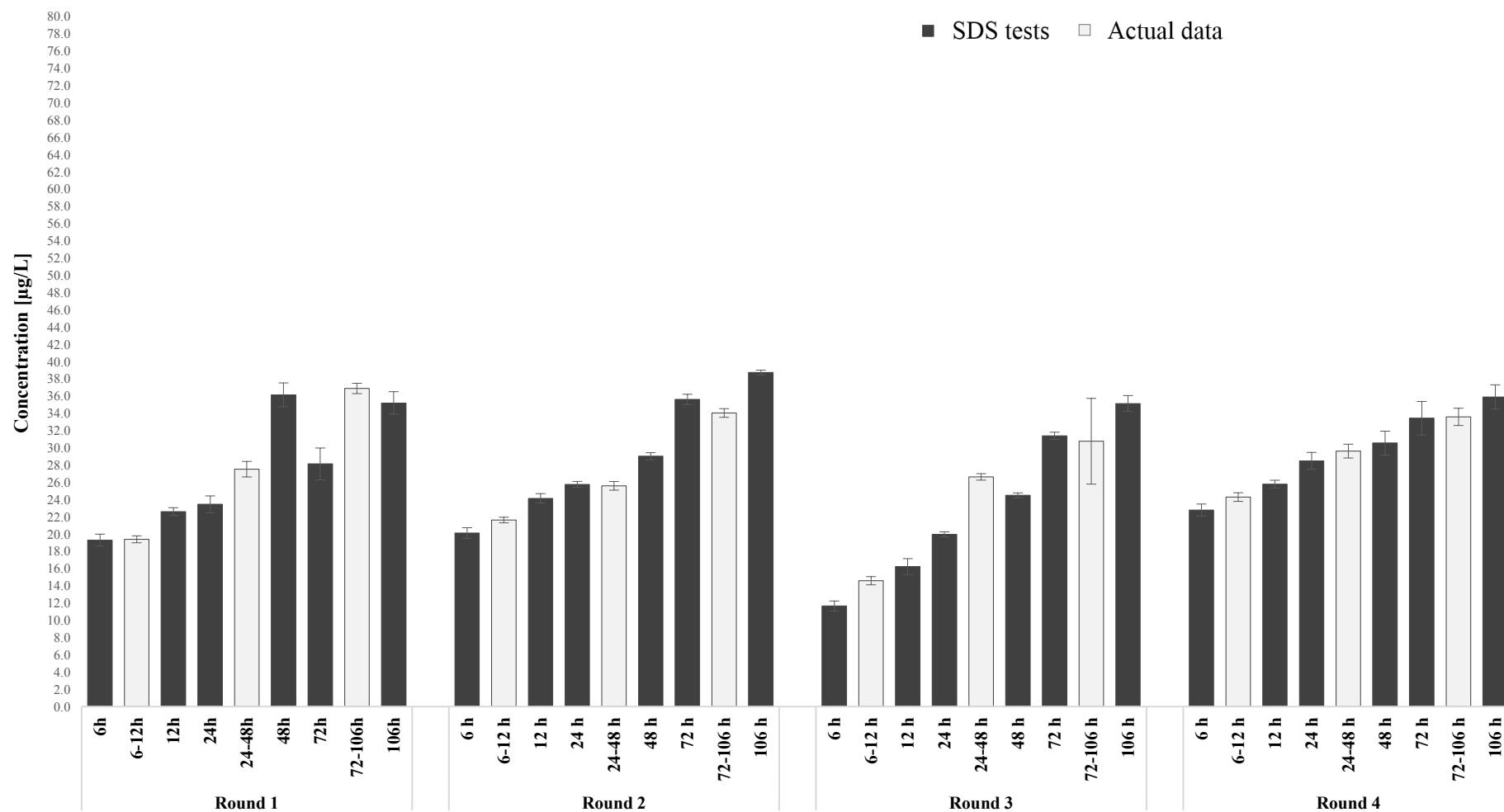


**Figure 5.18:** Total THMs (chloroform, BDCM, DBCM, bromoform) occurrence in SDS tests and actual distribution from chloraminated WTW D.

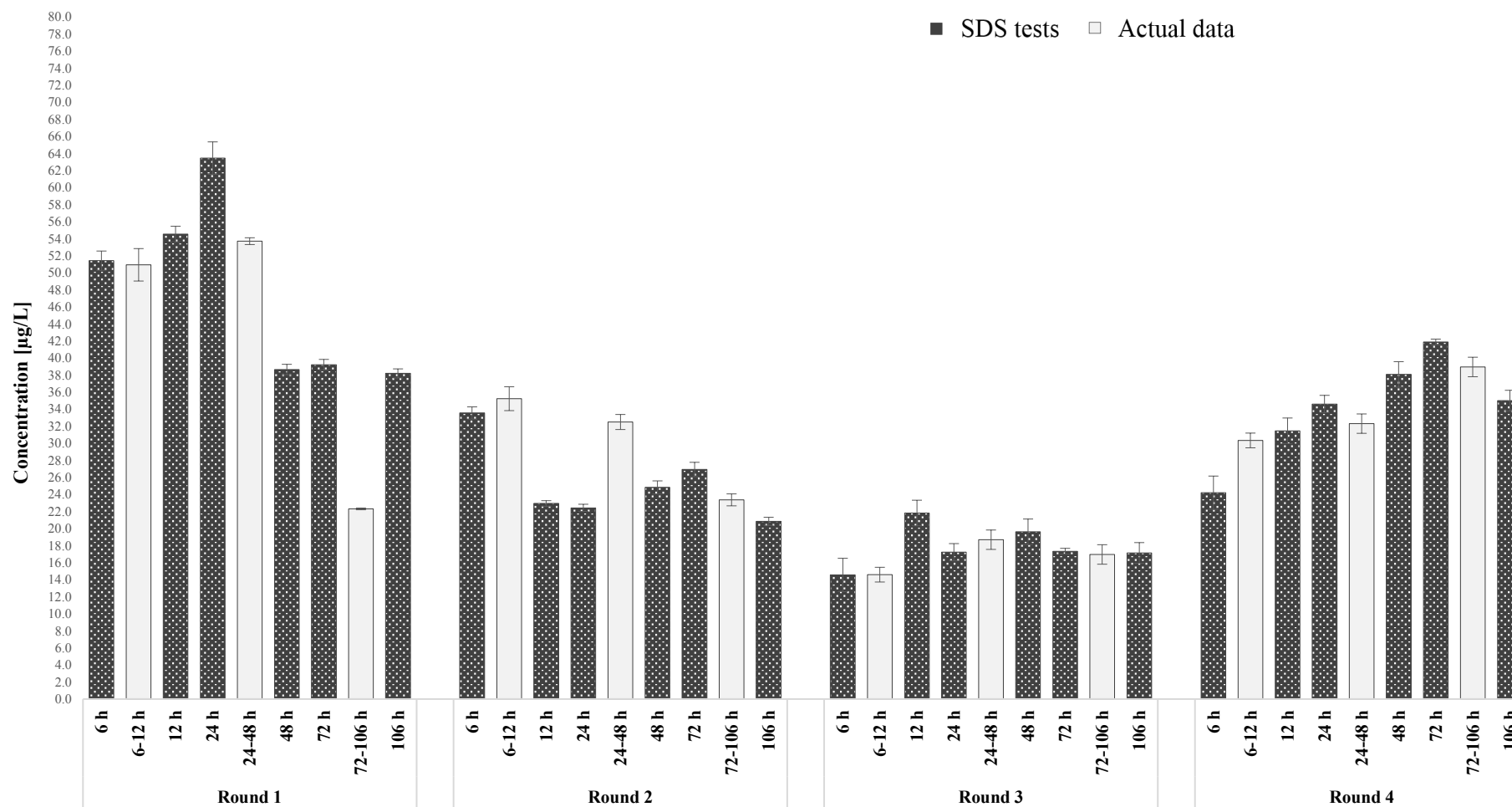


**Figure 5.19:** Total HAAs (MCAA, MBAA, DCAA, TCAA, DBAA, BCAA, BDCAA, DBCAA, TBAA) occurrence in SDS tests and actual distribution from chlorinated **WTW C**.

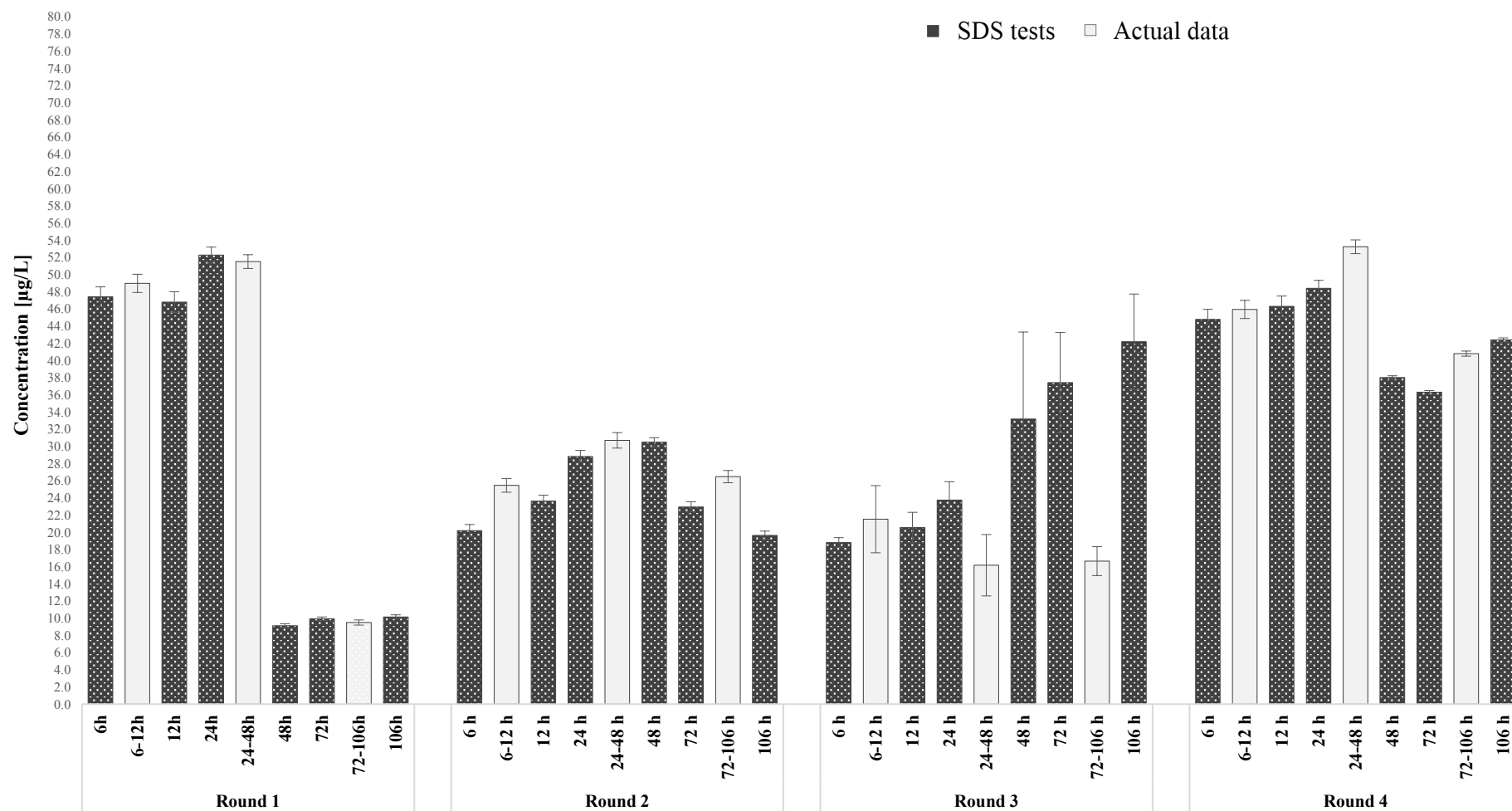


**Figure 5.20:** Total HAAs (MCAA, MBAA, DCAA, TCAA, DBAA, BCAA, BDCAA, DBCAA, TBAA) occurrence in SDS tests and actual distribution from chlorinated **WTW D**.

### 5.2.2.3 Haloacetonitriles (HANs) in chloraminated SDS tests

The SDS test effectively estimated the formation and degradation of both target N-DBP classes, HANs and HAcAms in the selected chloraminated systems. The levels of N-DBPs reported from the SDS were statistically similar with those quantified in the actual distribution samples during all sampling rounds, and their concentration scale was significantly lower than that of THMs and HAAs. Once more, from the seven selected HANs, only five of them were identified, whereas from the nine HAcAms, eight were identified with the analytical methods applied. The total HAN concentrations reported by the chloraminated SDS tests were  $< 4 \mu\text{g/L}$  with a median value of  $1.7 \mu\text{g/L}$  (*median in actual:  $1.0 \mu\text{g/L}$* ) and  $2.1 \mu\text{g/L}$  (*median in actual:  $1.9 \mu\text{g/L}$* ), in WTW C and D, respectively. **Figures 5.21** and **5.22** show the fate of HANs levels in the chloraminated simulated distribution system tests in comparison with those reported from the actual distribution locations as a function of the water age. These figures demonstrate that HANs occurrence was low during chloramination (Templeton et al. 2012) and that most of the total HAN concentrations identified in actual systems were found to be between the concentrations identified in the lower and upper limits of their water age ranges, expressed as incubation times in SDS tests. However, several exceptions were observed especially in low and medium water ages, where HAN levels in SDS tests were slightly higher (*median deviation: 40%*) than those identified in the actual networks during the same water ages. Nevertheless, from a practical viewpoint these deviations were small between the two set of samples, with the maximum deviation reported in WTW C being  $0.8 \mu\text{g/L}$  during Round 2. This overestimation was likely due to the different circulation and/or mixing conditions in the SDS bottles that may have enhanced HANs formation or delayed HANs hydrolysis. The potential impact of other parameters for this overestimation in SDS tests was possible but not wholly confirmed by the detailed database (*Appendix B.9-B.16*); low pH ( $< 7$ ) reported to enhanced HANs stability (UK WIR 2014), or lower disinfectant residual in actual distribution enhanced HANs hydrolysis (Krasner et al. 2011). This tendency has been previously reported in chloraminated SDS tests of a US occurrence study (Weinberg et al. 2002) and in SDS tests that were characterised by nitrification phenomena (Zeng and Mitch 2016).

Generally, it was observed that similarly chlorinated SDS tests, HANs concentrations increased between the lowest (6 hours) and the highest incubation time (106 hours), in all chloraminated SDS samples, with varying increase rates; ranging from 6% to 52%. This has been previously reported during chloramination experiments by Yang et al. (2007), where the effect of contact time was investigated and concluded that HANs presented an increase between 0 and 170 hours of incubation. Although the overall increases in the

current study, HAN levels presented decays during the intermediate incubation times. These decays were mainly identified around 48-72 hours and 24-48 hours in WTW C and D, respectively, were not significant to influence the occurrence of total HAN. Even though a generalised pattern concerning the behaviour of HANs in chloraminated distribution systems cannot be proposed, the median values from the SDS tests suggested that total HANs increased until 24 hours in WTW C and until 12 hours in WTW D. That was followed by a decrease until 72 hours and 48 hours, in the two different WTW, respectively, due to hydrolysis (Glezer et al. 1999; Bond et al. 2015), with a subsequent increase until 106 hours. The same pattern was observed by Chen and Weisel (1998) in their chloraminated SDS tests, where HAN levels (3 *species*) were reported to increase until 24 hours, with a subsequent decrease until 72 hours. Also, HANs occurrence was not characterised by any seasonal variability in chloraminated systems, since similar levels were identified in low and high water temperature incubations. This observation suggested that the HANs generation was affected by the combining effect of the water matrix constituents, and the environmental conditions (temperature, pH), during each sampling round (Nikolaou et al. 2000; Weinberg et al. 2002; Bond et al. 2012).

Furthermore, SDS tests were proven to be a useful tool to predict the speciation of HANs in the distribution networks. Since the two chloraminated systems were characterised by a significant difference in bromide levels (*median in C: 82 µg/L; median in D: 19.9 µg/L*), this affected considerably the speciation. Similar to the actual chloraminated samples, in the SDS tests of WTW C the most predominant HAN species were DBAN, followed by DCAN, whereas in SDS tests of WTW D the most abundant species was DCAN. During the four sampling rounds the brominated species represented 53% (*median*) and 16% (*median*) of the total HANs, in WTW C and D water samples, respectively. Even though in the SDS samples of WTW D the brominated species always represented the lowest fraction of total HANs, it was surprising that this was also observed in several samples of WTW C. This was more likely related to the statistical error occurred from the low or below detection limits occurrence of several species, representative of the bromine containing fraction. Indeed, in WTW C SDS samples that the chlorinated fraction was higher, MBAN was always below the detection limits, and DBAN and BCAN were reported to be either close or below the detection limits, which has influenced the statistical fractionisation of the results regardless of the bromide levels.

#### 5.2.2.4 Haloacetamides (HAcAms) in chloraminated SDS tests

A key question of this research was whether HAcAms formation and speciation can be predicted via the implementation of simulated distribution systems in chloraminated waters. It is already known that SDS tests have been successfully implemented to predict the occurrence of THMs, HAAs and 3 species of HANs (Koch et al. 1991), while in Chapter 5.2.1 it was discussed that SDS tests also predicted the formation of HAcAms in chlorinated systems. The validation of the SDS tests to represent the occurrence and speciation of HAcAms in chloraminated systems (WTW C and D) was performed by the comparison between the data generated from the incubation bottles (*representing actual water ages*) and the actual distribution location. These results are summarised in **Figures 5.23** and **5.24**, which illustrate that the predicted and actual total HAcAms levels as a function of water ages, in the chloraminated WTW C and D systems, respectively. From these graphs, it was initially observed that the simulation of HAcAm levels and behaviour in actual chloraminated systems was highly represented by the SDS of WTW C and D. Even though the generation of HAcAms was not following any temporal and seasonal pattern among the sampling events, the SDS tests succeeded in capturing all the different scenarios over the same amount of time and temperature. If an exception was to be noted, it would be the tendency of some SDS samples to have slightly overestimated the levels of HAcAms, with deviations ranging 0.2-2 µg/L between the different sample sets (maximum in *WTW C, Round 3, 72-106 h*). The majority of this tendency was observed in samples that represented high water ages (72-106 h), and was possibly related with the combination of competing and complex formation and degradation reactions, and hydraulics occurring at this stage of distribution (AWWA 2002). This observation, however, was the exact opposite phenomenon in chlorinated systems, where SDS seemed to underestimate the occurrence of HAcAms in high water ages. Even though literature does not provide any explanation to this tendency, and the incubation bottles were isolated from the known factors that may trigger HAcAm in distribution pipes (pipe corrosion, organic materials in pipe walls), it was possible that the inorganic nitrogen incorporation was elevated (Yang et al. 2010). The fact that chloramines were circulating in a confined space, may have enhanced inorganic nitrogen incorporation against that occurring in the actual water networks. This was not possible to be evaluated during this study since isotopically labelled monochloramine was not used in the experiments. In any case, the reported deviations were practically minimal, and it was concluded that SDS test predicted well the occurrence of HAcAms in chloraminated systems. Besides, from the data obtained, total HAcAm concentrations in SDS samples were always <7 µg/L in both chloraminated systems, with median values of 4.0 µg/L (3.9 µg/L in actual

*distribution samples*) and 3.6 µg/L (3.7 µg/L in *actual distribution samples*), in WTW C and D, respectively. As previously mentioned, there was no consistent relationship between the fate of HAcAms in distribution systems and seasonal and/or temporal variation in both chloraminated systems, as in the chlorinated ones. Generally, HAcAm concentrations in WTW C and D were increasing between 6 and 106 hours, in the same three of four sampling rounds (*Round 2, 3, 4*) by rates that were inversely proportional to water temperature, which was partially confirmed from actual distribution samples. More specifically, in WTW C, it was observed that the increase rate between the lowest incubation time (6 hours) and the highest incubation time (106 hours) was significantly higher (73%) during the period with the lowest water temperature (*Round 2~8°C*) than those calculated for Round 3 (*14°C*) and Round 4 (*22°C*), with increases 43% and 20%, respectively. Likewise, in WTW D, the increase rate in Round 2 was 41%, against those during Round 3 and 4 which were 19% and 9%, respectively. In addition, the intermediate concentration fluctuations of total HAcAms did not present any general temporal pattern. However, from the median levels reported in each water age during all sampling rounds, it was observed that total HAcAms followed an increase until 48 hours, with a subsequent degradation around 72 hours followed by a final increase until 106 hours. This HAcAms degradation, though, was not necessarily linked with consequent formation of their relative HAAs, while HAcAms increase was partially linked with HANs hydrolysis. Since this was observed in both chlorinated and chloraminated systems, it indicated that the formation of HAcAms was associated with nitrogen and non-nitrogen organic precursors found in the samples water matrices (Yang et al. 2010; Chuang et al. 2015; Chu et al. 2016), and could form independently from HANs (Huang et al. 2012). Furthermore, HAcAms formation in chloraminated waters was not characterised by any seasonal pattern (expressed in water temperature), since the occurrence in 8°C was similar with that observed in 22°C (Bond et al. 2011; Templeton et al. 2012). Therefore it was concluded that the formation of HAcAms was mainly influenced by the nature of the organic constituents in the water matrices rather than the water quality conditions in the incubation bottles.

Another point of interest in this study was the prediction of the HAcAms speciation in chloraminated systems via the implementation of SDS tests. When the actual distribution results were compared with those identified in the incubation bottles, the weight ratios of bromine containing HAcAms species were very similar, averaging 81% (86% in *actual distribution*) and 66% (70% in *actual distribution*) during the various incubation times, in WTW C and D SDS samples, respectively. The above percentages highlighted once more the importance of bromide, even in low concentrations as found in WTW D, in the

preponderance of brominated HAcAms in distribution systems. In the same way, as in the actual distribution samples of WTW C and D, the most abundant HAcAms species were DBAcAm, DCaAcAm and BCaAcAm. Finally, it was noteworthy that in both chloraminated systems, regardless of the bromide level, DCaAcAm occurred at similar levels to DCAN, with respective median values of 0.7 µg/L and 0.6 µg/L in WTW C, and respective median values of 1.1 µg/L and 1.3 µg/L in WTW D. This observation, initially reported by Krasner et al. (2006), was further evidence of the SDS tests performance to simulate N-DBPs in distribution.

Overall, it was observed that SDS test results encompassed the ranges of HANs and HAcAms concentrations and speciation expected to be identified during the different water ages within the chloraminated distribution systems. Total HAN concentrations were significant lower than those generated in chlorinated systems and the levels predicted to generate in the early stages of distribution are similar or slightly higher (*by 0.1- 1.7 µg/L*) at the final stages, regardless of the intermediate increases and decreases, thus were increasing with time. Total HAcAm concentrations that were predicted to generate in chloraminated systems did not present any significant spatial and/or temporal pattern, however it seemed to increase between 6 and 106 hours. From a practical standpoint, though, the implementation of SDS in chloraminated systems will accurately predict the occurrence and fate of HANs, and to a better extent of HAcAms in their systems.

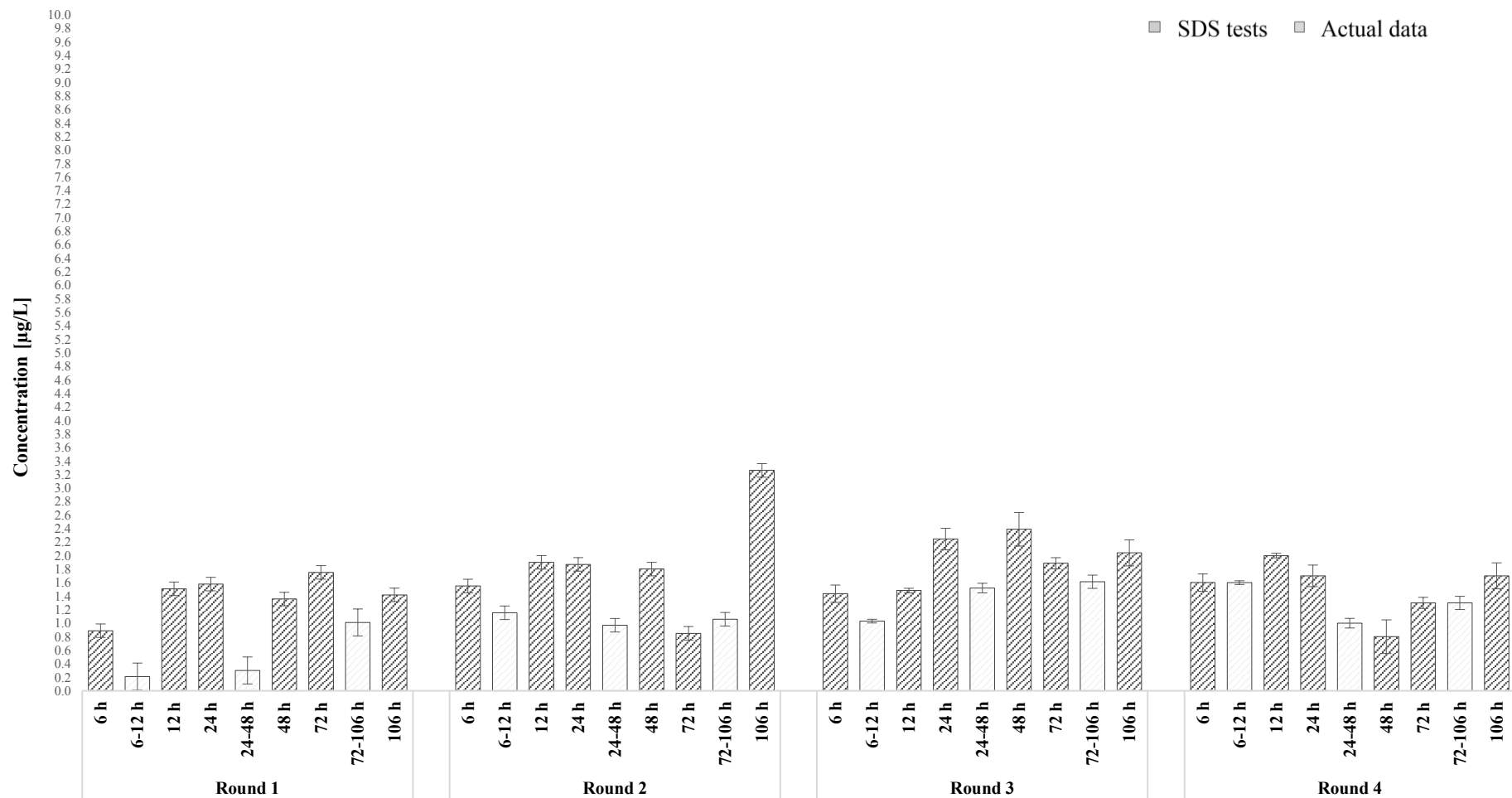


**Figure 5.21:** Total HANs (MCAN, MBAN, DCAN, TCAN, DBAN, BCAN, BDCAN, DBCAN, TBAN) occurrence in SDS tests and actual distribution from chlorinated **WTW C**.

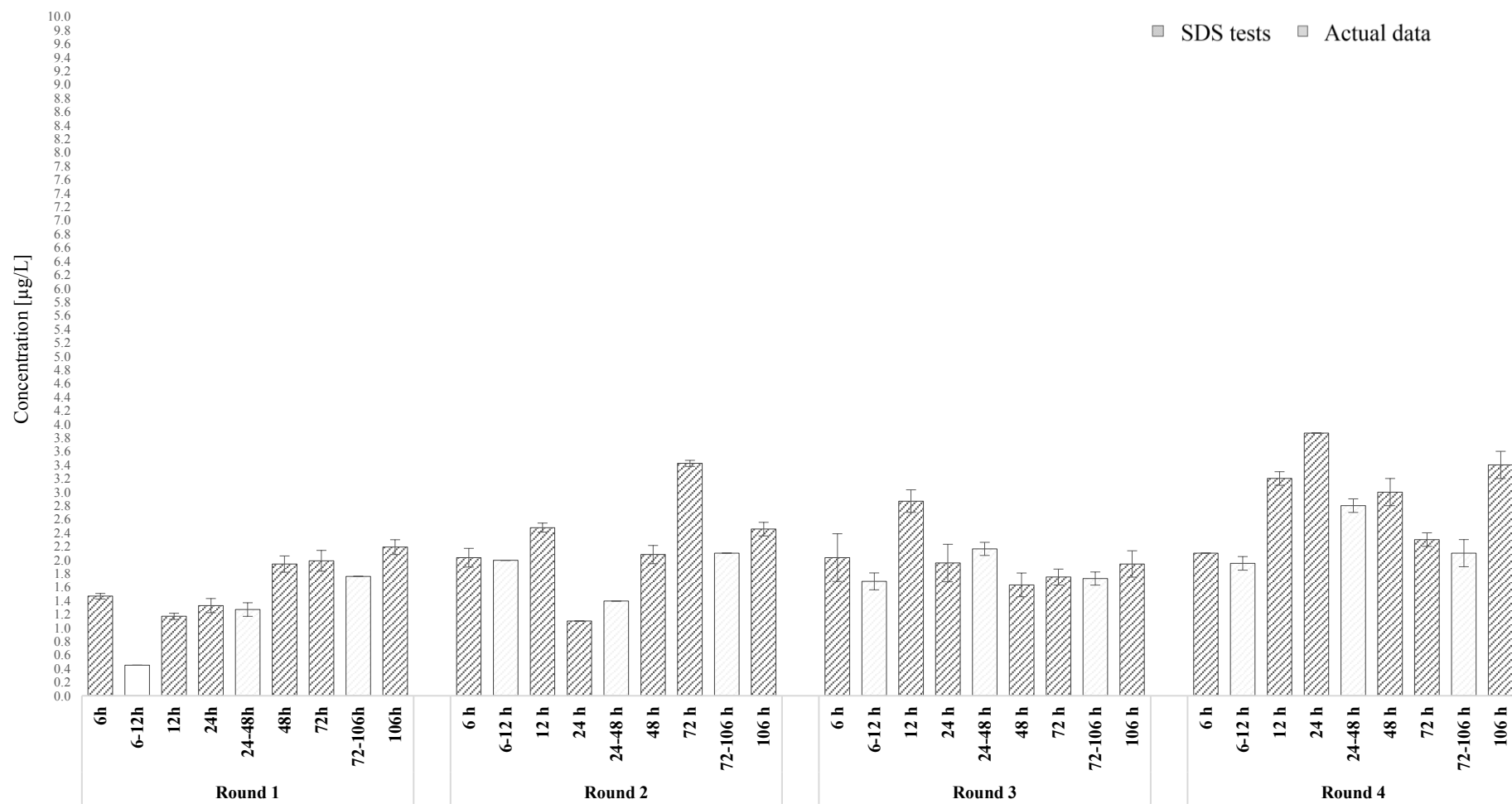


**Figure 5.22:** Total HANs (MCAN, MBAN, DCAN, TCAN, DBAN, BCAN, BDCAN, DBCAN, TBAN) occurrence in SDS tests and actual distribution from chlorinated **WTW D**.

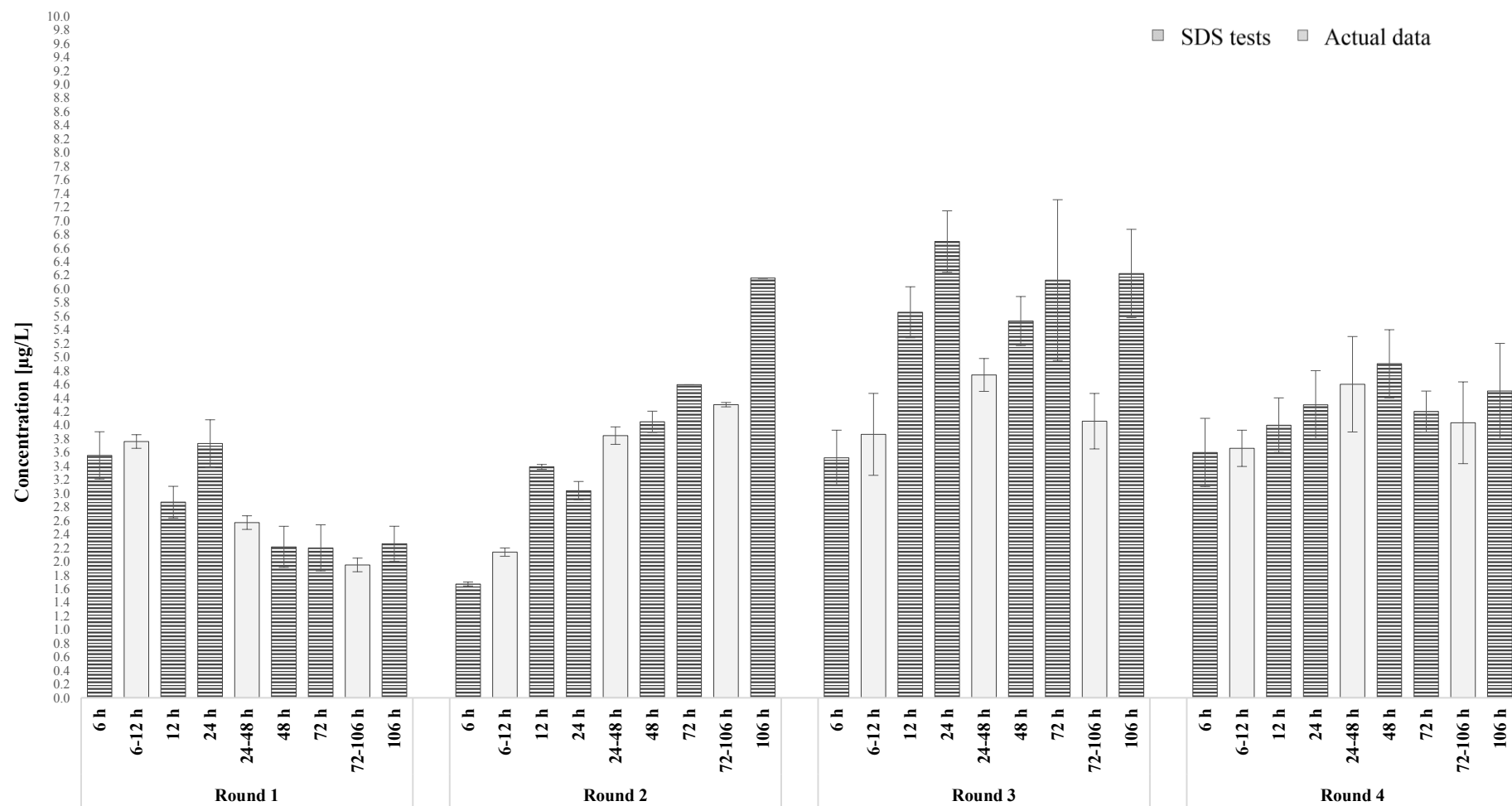


**Figure 5.23:** Total HAcs (MCAcAm, MBAcAm, DCAcAm, TCAcAm, DBAcAm, BAcAm, BDCAcAm, DBCAcAm, TBAcAm) occurrence in SDS tests and actual distribution from chloraminated WTW C.

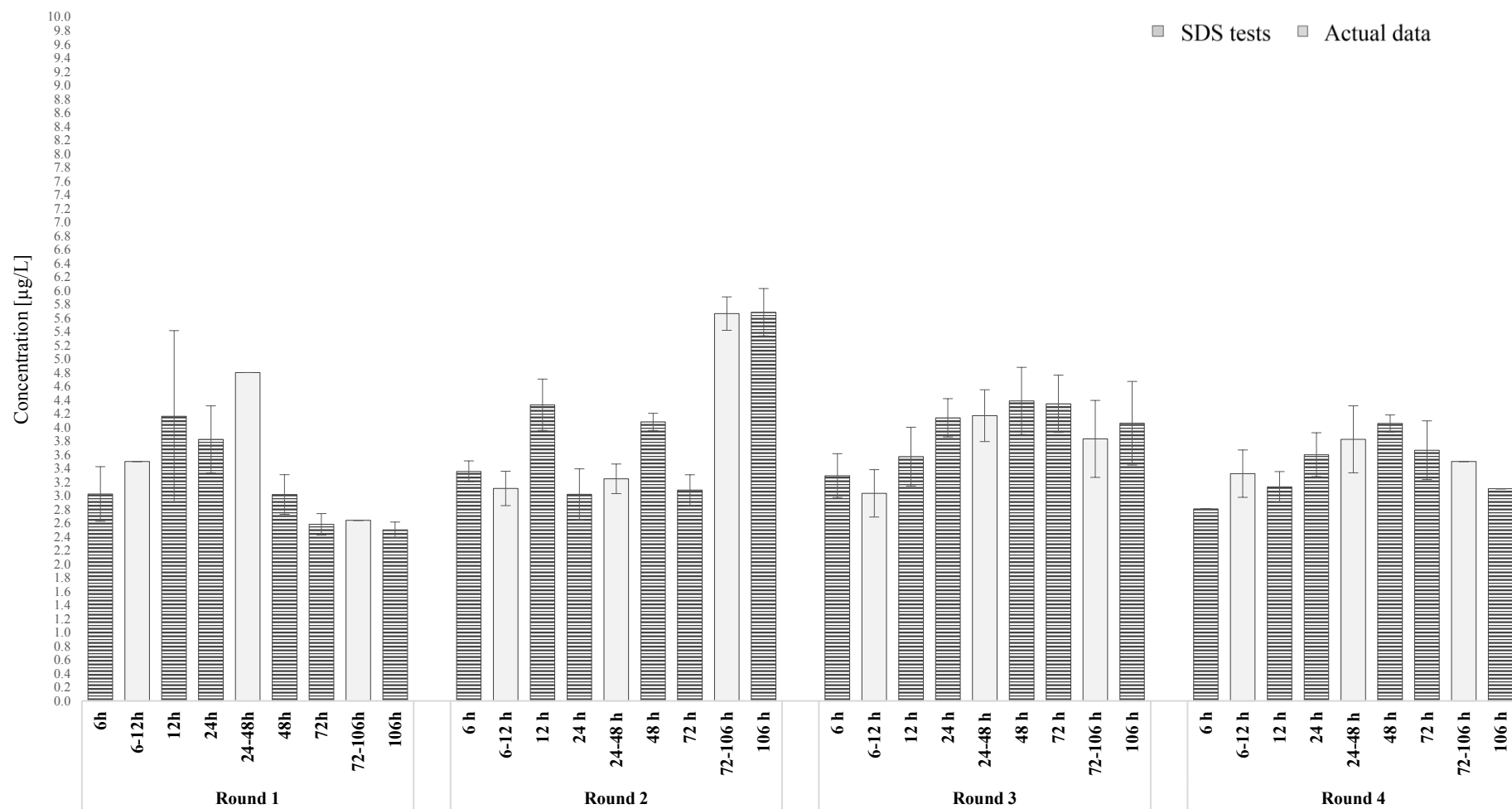


**Figure 5.24:** Total HAcAms (MCaAm, MBaAm, DCaAm, TCaAm, DBaAm, BCaAm, BDCAm, DBCaAm, TBaAm) occurrence in SDS tests and actual distribution from chlorinated D WTW.

### 5.2.3 Correlation between DBPs and water quality parameters in SDS tests

Since the database generated from the simulated distribution system tests was considerably larger and more detailed than the database of the actual distribution samples, it provided more solid observations and subsequently clearer correlations between the parameters of the study. Once more, the Pearson correlation coefficient ( $r$ ) was calculated to examine potential correlations between water quality and DBP concentrations in simulated chlorinated and chloraminated distribution system tests (**Tables 5.8 and 5.9**). The fact that the water samples incubated during the SDS tests were collected from real water treatment works limited the variability of several parameters such as pH, and disinfectant residual, already controlled by the water utilities. However, since SDS tests were implemented in four seasonal rounds enabled the correlations with other water quality parameters such as temperature, TOC, water age and of course between the various DBP groups.

As expected the most pronounced correlation in both chlorinated and chloraminated systems was that of total THMs with water age, with  $r$  values of 0.80 (0.85 in actual) and 0.88 (0.92 in actual), respectively. None of the other DBP classes presented a similar correlation with water age, even though the final concentrations previously discussed are indicative of the trends to be expected in distribution systems. Regarding trends between regulated THMs and other groups, the only correlations observed were those between chloroform and chlorine-containing HAAs in chlorinated systems ( $r=0.53$ ), and chloroform and chlorine-containing HANs ( $r=0.73$ ) in chloraminated systems.

Another important correlation observed was that of total DBPs concentrations and their relative bromine-containing species in chlorinated as well in chloraminated systems. This indicated that the brominated species of each target DBPs were highly responsible on the sum concentrations of the different DBP classes, regardless the bromide concentration. The only exception was observed in chloraminated systems where total HANs concentration presented poor correlation with their relative brominated HANs, linked with the elevated formation of TCAN. More specifically, in chlorinated systems the various DBP classes presented the following  $r$  values between their bromine containing species; 0.96 in THMs, 0.94 in HAAs, 0.60 in HANs and 0.66 in HAcAms. In chloraminated systems, the same correlation was weaker in the case of THMs ( $r_{THMs}=0.57$ ), similar in the case of HAAs ( $r_{HAAs}=0.91$ ), but more robust in the case of HAcAms ( $r_{HAcAms}=0.93$ ). The above agreed with Goslan et al. (2009) where it was reported that the incorporation of bromide in HAAs was unaffected by the disinfectant method, in contrast with the bromide incorporation of

THMs that was slightly decreased during chloramination. Yet, it is interesting that during chloramination the accumulation of bromine-containing HAcAms was primarily responsible for the yields of total HAcAms reported, whereas the same was not observed in the case of HANs. As such, even if HANs would hydrolyse to form their relative HAcAms in chlorination, the same would not have been possible in chloramination, at least with the brominated species according to the above trend. It is known from literature that HANs may hydrolyse to form HAcAms, which subsequently further hydrolyse to form HAAs (Glezer et al. 1999; Reckhow et al. 2001). In contrast with the brominated species, a correlation between Cl-HANs and Cl-HAcAms of  $r$  values 0.74 and 0.53 was reported in chlorinated and chloraminated samples, respectively, however no correlation was reported between HAcAms and HAAs. This indicated that the chlorine-containing species of the N-DBP groups had high probability to be complementary, and shared the same precursors. However, the absence of correlation between the total concentrations and Br-species of these classes indicated that simultaneous independent formation from different precursors was also possible.

Similarly, to the actual distribution samples, there was no correlation observed between the DBP occurrence in SDS samples and the water quality parameters, apart from water temperature and bromide. Thus, it was concluded that TOC, SUVA, UV absorbance and pH were considered poor indicators of regulated and unregulated DBPs in distribution (US EPA 2004). As far as the correlations between water temperature and DBPs were concerned, temperature correlated well mainly with total HAAs in all selected systems, since HAAs occurrence was considerably lower during cold water temperatures and the opposite. The fact that a similar strong correlation was not observed between THMs, was mainly due to that the variables were not completely independent, since monitoring was performed in real water matrices. Therefore, water samples obtained from different seasonal samplings apart from presenting different water temperatures were also characterised by different TOC levels, and organic constituents (Teixeira and Nunes 2011).

**Table 5.8:** Correlations\* between DBP groups and water quality parameters in chlorinated SDS tests (WTW A and B).

|                   | <i>Total THMs</i> | <i>CHCl<sub>3</sub></i> | <i>Br-THMs</i> | <i>Total HAAs</i> | <i>Cl-HAAs</i> | <i>Br-HAAs</i> | <i>Total HANs</i> | <i>Cl-HANs</i> | <i>Br-HANs</i> | <i>Total HAcAms</i> | <i>Cl-HAcAms</i> | <i>Br-HAcAms</i> |
|-------------------|-------------------|-------------------------|----------------|-------------------|----------------|----------------|-------------------|----------------|----------------|---------------------|------------------|------------------|
| Total THMs        |                   |                         |                |                   |                |                |                   |                |                |                     |                  |                  |
| CHCl <sub>3</sub> | <b>0.73</b>       |                         |                |                   |                |                |                   |                |                |                     |                  |                  |
| Br-THMs           | <b>0.96</b>       | <b>0.61</b>             |                |                   |                |                |                   |                |                |                     |                  |                  |
| Total HAAs        | 0.35              | 0.34                    | 0.26           |                   |                |                |                   |                |                |                     |                  |                  |
| Cl-HAAs           | 0.46              | <b>0.53</b>             | 0.39           | <b>0.84</b>       |                |                |                   |                |                |                     |                  |                  |
| Br-HAAs           | 0.24              | 0.20                    | 0.15           | <b>0.96</b>       | <b>0.65</b>    |                |                   |                |                |                     |                  |                  |
| Total HANs        | 0.39              | 0.41                    | 0.42           | -0.16             | 0.15           | -0.30          |                   |                |                |                     |                  |                  |
| Cl-HANs           | 0.48              | <b>0.50</b>             | <b>0.54</b>    | 0.36              | <b>0.51</b>    | 0.24           | <b>0.55</b>       |                |                |                     |                  |                  |
| Br-HANs           | -0.01             | -0.06                   | 0.01           | -0.38             | -0.32          | -0.37          | <b>0.60</b>       | -0.34          |                |                     |                  |                  |
| Total HAcAms      | 0.16              | 0.39                    | 0.13           | 0.09              | 0.30           | -0.03          | 0.49              | <b>0.60</b>    | -0.02          |                     |                  |                  |
| Cl-HAcAms         | 0.19              | 0.31                    | 0.24           | -0.04             | 0.22           | -0.17          | <b>0.50</b>       | <b>0.74</b>    | -0.12          | <b>0.78</b>         |                  |                  |
| Br-HAcAms         | 0.01              | 0.15                    | -0.08          | 0.06              | 0.09           | 0.03           | 0.31              | 0.06           | 0.28           | <b>0.66</b>         | 0.09             |                  |
| Temperature       | 0.46              | 0.36                    | 0.42           | <b>0.81</b>       | <b>0.82</b>    | <b>0.70</b>    | -0.08             | <b>0.57</b>    | -0.59          | 0.20                | 0.19             | -0.05            |
| pH                | 0.31              | <b>0.68</b>             | 0.13           | 0.26              | 0.50           | 0.13           | -0.05             | -0.09          | -0.11          | -0.04               | -0.25            | 0.09             |
| UV                | -0.44             | -0.83                   | -0.16          | -0.82             | -0.77          | -0.78          | 0.35              | 0.04           | 0.39           | 0.22                | <b>0.61</b>      | -0.06            |
| TOC               | -0.34             | 0.11                    | -0.46          | -0.25             | -0.01          | -0.32          | 0.05              | -0.05          | 0.00           | 0.09                | 0.11             | 0.02             |
| SUVA              | -0.30             | -0.73                   | 0.00           | -0.75             | -0.72          | -0.70          | 0.42              | 0.16           | 0.44           | 0.22                | <b>0.57</b>      | -0.05            |
| Residual          | -0.71             | -0.49                   | -0.71          | -0.21             | -0.16          | -0.23          | -0.41             | -0.62          | -0.30          | 0.17                | 0.32             | -0.08            |
| Water age         | <b>0.80</b>       | <b>0.52</b>             | <b>0.79</b>    | -0.04             | -0.01          | -0.06          | 0.39              | 0.17           | 0.34           | -0.02               | 0.00             | 0.01             |
| Bromide           | -0.64             | -0.78                   | -0.61          | -0.96             | -0.96          | -0.95          | <b>0.62</b>       | -0.71          | <b>0.83</b>    | 0.19                | -0.17            | <b>0.63</b>      |

\*Pearson product moment correlation coefficient.

**Table 5.9:** Correlations\* between DBP groups and water quality parameters in chloraminated SDS tests (WTW C and D).

|              | <i>Total THMs</i> | <i>CHCl<sub>3</sub></i> | <i>Br-THMs</i> | <i>Total HAAs</i> | <i>Cl-HAAs</i> | <i>Br-HAAs</i> | <i>Total HANs</i> | <i>Cl-HANs</i> | <i>Br-HANs</i> | <i>Total HAcAms</i> | <i>Cl-HAcAms</i> | <i>Br-HAcAms</i> |
|--------------|-------------------|-------------------------|----------------|-------------------|----------------|----------------|-------------------|----------------|----------------|---------------------|------------------|------------------|
| Total THMs   |                   |                         |                |                   |                |                |                   |                |                |                     |                  |                  |
| Chloroform   | 0.50              |                         |                |                   |                |                |                   |                |                |                     |                  |                  |
| Br-THMs      | <b>0.57</b>       | -0.43                   |                |                   |                |                |                   |                |                |                     |                  |                  |
| Total HAAs   | -0.07             | -0.02                   | -0.06          |                   |                |                |                   |                |                |                     |                  |                  |
| Cl-HAAs      | -0.02             | 0.22                    | -0.23          | 0.34              |                |                |                   |                |                |                     |                  |                  |
| Br-HAAs      | -0.07             | -0.11                   | 0.04           | <b>0.91</b>       | -0.08          |                |                   |                |                |                     |                  |                  |
| Total HANs   | 0.31              | <b>0.53</b>             | -0.18          | -0.16             | 0.13           | -0.22          |                   |                |                |                     |                  |                  |
| Cl-HANs      | 0.35              | <b>0.73</b>             | -0.33          | -0.33             | 0.21           | -0.45          | <b>0.77</b>       |                |                |                     |                  |                  |
| Br-HANs      | -0.07             | -0.34                   | 0.25           | 0.28              | -0.12          | 0.35           | 0.27              | -0.41          |                |                     |                  |                  |
| Total HAcAms | 0.21              | -0.22                   | 0.43           | -0.26             | -0.13          | -0.22          | 0.08              | 0.13           | -0.08          |                     |                  |                  |
| Cl-HAcAms    | 0.15              | 0.39                    | -0.22          | -0.09             | 0.26           | -0.21          | 0.29              | <b>0.53</b>    | -0.39          | 0.47                |                  |                  |
| Br-HAcAms    | 0.17              | -0.41                   | <b>0.57</b>    | -0.25             | -0.26          | -0.15          | -0.03             | -0.08          | 0.08           | <b>0.93</b>         | 0.11             |                  |
| Temperature  | 0.06              | 0.13                    | -0.06          | 0.45              | -0.10          | <b>0.52</b>    | 0.03              | -0.14          | 0.26           | -0.13               | -0.07            | -0.12            |
| pH           | 0.09              | -0.24                   | 0.31           | -0.43             | 0.09           | -0.50          | 0.27              | 0.21           | 0.08           | 0.31                | -0.05            | 0.37             |
| UV           | -0.05             | -0.03                   | -0.03          | -0.08             | 0.28           | -0.21          | 0.21              | 0.18           | 0.02           | 0.07                | 0.04             | 0.07             |
| TOC          | 0.10              | 0.00                    | 0.11           | -0.04             | 0.19           | -0.12          | -0.14             | -0.18          | 0.06           | -0.16               | -0.36            | -0.03            |
| SUVA         | -0.09             | -0.05                   | -0.04          | -0.01             | 0.02           | -0.02          | 0.18              | 0.18           | -0.01          | 0.14                | 0.24             | 0.06             |
| Residual     | -0.77             | -0.33                   | -0.49          | -0.36             | 0.00           | -0.35          | -0.21             | -0.15          | -0.08          | -0.10               | -0.20            | -0.04            |
| Water age    | <b>0.88</b>       | 0.29                    | <b>0.64</b>    | -0.17             | -0.06          | -0.15          | 0.19              | 0.23           | -0.07          | 0.22                | 0.15             | 0.18             |
| Bromide      | -0.05             | -0.79                   | <b>0.62</b>    | 0.12              | 0.06           | 0.10           | -0.21             | -0.59          | <b>0.53</b>    | 0.13                | -0.59            | 0.40             |

\*Pearson product moment correlation coefficient.

### 5.3 The effect of disinfection method alteration on DBP formation

The implementation of alternative disinfection methods, and more specifically switching from chlorine to chloramines, has been a widely proposed strategy to effectively control the formation of regulated DBPs in drinking water (US Environmental Protection Agency 2010). Despite the observed positive effects of chloramines compared to chlorine on the formation of THMs and HAAs, many studies postulate that the implementation of chloramines may aid unintended reactions and encourage the formation of nitrogenous DBPs (Krasner et al. 2006), or induce other side effects (e.g. promote the formation of Br-HAAs, impact di-HAAs) (Cowman and Singer 1996; Diehl et al. 2000).

A fundamental question posed by this research project was the simultaneous investigation of the effect of disinfectant method alteration on the formation and fate of regulated and unregulated DBPs in distribution, and in particular whether the addition of nitrogen in to the water during chloramination to reduce THM and HAA formation might concurrently increase N-DBP concentrations. The validation of the simulated distribution system (SDS) tests (**Chapter 5.2**) as a useful tool to predict the behavior of DBPs in distribution allowed the impact assessment of disinfectant alteration in the same systems. Therefore, water samples from WTW A and B, usually chlorinated by the water utility, were chloraminated and incubated in the laboratory to simulate the occurrence of DBPs at the same water ages and water quality conditions, selected for the initial SDS tests. Likewise, water samples from WTW C and D, usually chloraminated by the water utility, were chlorinated in the laboratory and incubated for the same water ages. This work package facilitated the direct comparison of DBP levels to be expected in the same distribution system, between the current disinfection practice and the potential alternative practice. The findings of this study not only provided a useful insight on operational strategies for regulatory compliance, but also contributed in the ongoing dialogue on whether the application of chloramines promote N-DBPs formation while minimizing THMs and HAAs.

It has to be noted that the chloramination mode in the treatment works was different than that in the laboratory experiments; water utilities pre-chlorinate water for approximately 30 minutes and then add ammonia (*in line chloramines*) whereas in the lab monochloramine solution was prepared prior to disinfection (*pre-formed chloramines*). Unfortunately, there is limited literature on the effect of chloramination modes on the formation of this study's target DBPs. Yang et al. (2007) examined the formation of chloroform and DCAN under four different chloramination scenarios, and postulated that

concentrations of chloroform varied among the different applications whereas the levels of DCAN remained stable. Another study by Qi et al. (2004), investigated the HAAs formation between the two chloramination modes and concluded that HAA levels were higher with in line chloramines, but only during the initial stages of disinfection. Since, the commonly chlorinated systems WTW A and B were chloraminated in the laboratory with pre-formed chloramines, for the purposes of the current investigation, if these systems switch to chloramines THMs and HAAs are expected to be more elevated in reality especially during low water ages, whereas HANs are expected to remain the same. A more representative comparison will be provided from the results of WTW C and D, since both chlorination and chloramination were performed similarly to the water utilities' practice.

Overall, switching from chlorine to chloramines in both WTW A and B systems, formed **lower** THMs, HAAs, HANs and HAcAms levels during all the sampling rounds that it was performed. Representative graphs of the DBP yields predicted to occur during chlorination and chloramination in WTW A and B can be found in **Figures 5.25** and **5.26**, respectively. Likewise, switching from chloramines to chlorine in WTW C and D systems, formed **higher** DBPs levels during all the sampling rounds. The results of this comparison between the DBP yields during chlorination and chloramination of C and D WTW are summarised in **Figures 5.27** and **5.28**, respectively. To the author's knowledge, this is the first time that real water samples have been directly compared on their response during both chlorination and chloramination, with regards to their potential in generating THMs, HAAs, HANs and HAcAms at the same time in distribution systems.

### 5.3.1 Switching from chlorine to chloramines

Overall, switching from chlorine to chloramines in both WTW A and B systems, formed **lower** THMs, HAAs, HANs and HAcAms levels during all the sampling rounds that it was performed. These findings were expected as chloramination is known to control THM and HAA formation when compared with chlorination (Hua and Reckhow 2007; Goslan et al. 2009). The novelty of these findings lay in the fact that chloramination was proven to also limit the formation of both HANs and HAcAms. Therefore, this was an indication that the nitrogen atom in N-DBPs came primarily from the organic nitrogen present in the water matrices, rather than from the ammonia added during chloramination.

In more detail, switching from chlorine to chloramines in WTW A, reported median decreases of 30% in THMs, 47% in HAAs, 72% in HANs and 55% in HAcAms. Switching from chlorine to chloramines in WTW B, reported median decreases of 36% in THM, 50% in HAAs, 50% in HANs and 47% in HAcAms. **Figure 5.25** and **5.26** summarise the results segmented by secondary disinfectant type, water age and season in WTW A and B, respectively. These findings agreed with previous studies that have investigated THMs, HAAs and HANs formation when using pre-formed chloramines, with typical reductions of 90%, 77% and 80%, respectively (Cowman and Singer 1996; Guay et al. 2005; Hua 2007; Bougeard et al. 2010).

When chlorine was used as the disinfectant, considerable variation was observed between the increase levels of **THMs** during each water age, with median concentration 44.7 µg/L (range: 19.5-75.4 µg/L) between 6 to 106 hours during all sampling rounds, whilst when chloramines were applied to the same water matrix THM median concentration was 30.5 µg/L (range: 16.5-55.3 µg/L) from 6 to 106 hours. Practically, this means that a potential switching to chloramines will not only decrease the total THM concentration in specific water ages but also will delay their formation; something that is important in large water networks with water ages exceeding 106 hours to achieve regulatory compliance. An unexpected decrease in total THMs formation (*of 4.5%*) was observed between 72 and 106 hours in the chloraminated SDS samples of WTW A. Singer et al. (1993) had previously reported transformation of THMs in anoxic conditions, possibly occurring in the incubation bottles used during this experiment at high retention times. Furthermore, it is important to note that the percentage of incorporated bromide in THMs was similar if not identical in several water ages during both chlorination (*median: 86%*) and chloramination (*median: 87%*) of the selected water matrices, regardless of the concentration deviations. This highlighted that, even though the alteration of disinfectant provided a significant minimisation of the regulated DBPs, optimal results would have been observed with bromide removal during water treatment. More specifically, the use of

chlorine in systems A and B showed that water utilities internal limits ( $<50 \mu\text{g/L}$ ) would be exceeded at 48 hours of retention time especially during warm months; switching to chloramines showed that these limits would have been exceeded only after 106 hours with water temperatures  $>20^\circ\text{C}$ . Potentially, even this outcome would have been avoided with further control of the bromide levels in finished water, since bromine containing species are responsible of more than three quarters of the total THM levels and/or optimized coagulation to remove precursors. However, to date there are no reliable methods for bromide removal in drinking water and future research may contribute to this.

Concerning the response of **HAAs**, a similar trend was reported as observed for THMs in that concentrations at chlorinated waters were significantly higher when compared to those using chloramines. However, the percentage of minimisation in total HAAs formation by switching to chloramines from chlorine was more significant (*median reduction: 50%*) than that of THMs (*median reduction: 37%*). Namely, median HAAs levels during chlorination were  $41 \mu\text{g/L}$  and  $28.4 \mu\text{g/L}$  in WTW A and B, respectively, whereas during chloramination under the same spatial and temporal conditions were  $14.5 \mu\text{g/L}$  and  $13.3 \mu\text{g/L}$ . It was noteworthy that regardless the considerable variance in HAAs occurrence between the two selected systems during chlorination, this variance was narrowed during chloramination. Furthermore, it was observed that the HAAs concentrations generated during the lowest incubation time (6 hours) were similar or slightly higher with those that occurred in the highest incubation time (106 hours), regardless of the intermediate occurrence variations during *both disinfection practices*. The above was previously the reported behavior of HAAs in chlorinated SDS tests (*Chapter 5.2.1*), however, according to the findings of the chloraminated SDS tests of WTW C and D (*Chapter 5.2.2*) it was an unexpected outcome. This observation indicated that the fate of HAAs in distribution systems cannot be simply explained by the chlorine chemistry involving ammonia but was likely related to site specific issues attributable to the combining effect of water quality constituents and conditions. However, if a limit of  $40 \mu\text{g/L}$  for total HAAs was selected, the implementation of chloramines in systems A and B would generate HAAs yields safely below this value, which is exceeded with the current disinfection method, especially during warm months. Moreover, the impact on HAAs speciation during chloramination has been widely studied with researchers suggesting that switching from chlorine to chloramines will be followed by a switch in speciation towards dihalogenated HAAs (Diehl et al. 2000; Krasner et al. 2008). The data obtained in this work package agreed partially with the literature in that there are usually similar levels of di- and tri-HAAs in chlorinated systems with di-HAAs being the most dominant group identified in chloraminated

systems (Cowman and Singer 1996). There were many exceptions to this rule, especially in WTW A where di-HAAs were the major species in chloraminated samples only in one of the three sampling events, whilst tri-HAAs were the dominant species during the other two. This unusual behavior may be attributable to the ability of ozonation in the treatment works to have efficiently removed important di-HAAs precursors (Hua and Reckhow 2007), mainly of non humic and hydrophilic character (Ates et al. 2007). Even so, the di-HAAs formed during chlorination were substantially higher than those formed during chloramination, by approximately 57%, in line with a similar study by Hua and Reckhow (2007) where this difference was calculated to be 30%. In addition, the percentage of brominated HAAs species was more elevated in chloraminated samples than in chlorinated by approximately 9%, which indicated that *the implementation of chloramines enhanced bromide incorporation in total HAAs*. Indeed, during chlorination the calculated median BIF was 0.35 while during chloramination was 0.43. This increased incorporation during chloramination was basically identified due to increased bromide substitution in the tri-HAAs species, with median BIF 0.50 in chlorination and 0.55 in chloramination, rather than in the di-HAAs species, with median BIF=0.55 during both disinfection practices.

The effect of applying chloramines as a disinfectant was similarly pronounced for **HANs** (*Figure 5.25-c* *Figure 5.26-c*) and **HAcAms** (*Figure 5.25-d* and *Figure 5.26-d*), and all N-DBP levels were lower than those identified with chlorination during all sampling events that this comparison occurred. In WTW A the median concentration of HANs changed from 4.1 µg/L in chlorinated to 1.1 µg/L when using chloramines, whereas median concentration of HAcAms changed from 4.1 µg/L to 1.6 µg/L. The maximum total HANs concentration observed during chloramination (4.1 µg/L) was approximately two times less than the maximum identified during chlorination (8.7 µg/L), identified both in Round 4 at 72 hours. Likewise, in WTW B the median concentration of HANs changed from 4.3 µg/L in chlorinated to 1.8 µg/L when using chloramines, whereas median concentration of HAcAms changed from 4.1 µg/L to 2.5 µg/L. Also, it was noteworthy that dominant species quantified during chlorination, such as DCAN and DBAN, were below the detection limits in several water ages during chloramination, which explained the low occurrence of N-DBPs. Overall, the results were comparable to the English nationwide occurrence survey where the use of chloramines was reported to also limit N-DBPs formation with similar median values of 1.5 µg/L for HAN and 3.8 µg/L for HAcAm (Templeton et al. 2012). In a study by a different research group in the UK by Goslan et al. (2009) reported HANs median levels of 1.3 µg/L in chloraminated waters. It has to be highlighted though that in the above-mentioned surveys, the impact of disinfection method in the

occurrence of DBPs was performed in waters sampled from different treatment plants which therefore presented different raw water and treatment characteristics. The simultaneous disinfection of the same real water samples with the actual and the alternative disinfectant via the implementation of SDS tests in this study though, enabled the direct comparison between the disinfection methods on the occurrence of DBPs and consists an important novelty.

Furthermore, knowledge on the impact of HANs and HAcAms speciation during chlorination is sparse (Bond et al. 2015) and during chloramination is even more limited. From the results of this study it was observed that the speciation was shifting towards the dihalogenated HANs and dihalogenated HAcAms during both chlorination and chloramination, whereas trihalogenated N-DBPs occurred always in lower levels. Thus, switching from chlorine to chloramines is expected to form less N-DBPs but without any considerable alteration in halogenation levels. However, it was observed that the application of chloramines altered the configuration of the abundant HANs species in both selected systems; from DBAN during chlorination to DCAN (WTW A) and TCAN (WTW B) during chloramination, due to the dramatic decrease of DBAN during chloramination. This was confirmed by the calculated percentage of brominated HANs, which shifted to more chlorine containing species during chloramination, since during chlorination bromide containing species represented approx. 80% of total HANs yields whereas during chloramination represented only the 12%. Such a pattern was not observed in the case of HAcAms where BCACAm, followed by DCAcAm remained the dominant HAcAms species during both disinfection processes. The percentage of bromine-containing HAcAms species was higher than that of chlorine-containing species during all water ages, with minimal variances between the two disinfection practices but with a tendency of slightly higher bromide incorporation during chloramination. In more detail, bromine containing HAcAms represented approx. 58% of total HAcAms yields in chlorination and 62% in chloramination. The implementation of chloramines was proven to encourage bromide incorporation only in HAcAms, in both di- and tri-HAcAms, with BIF=0.3 during chlorination that increased to 0.4 during chloramination.

Even if chloramines had the potential to limit the formation of N-DBPS, the occurrence of HANs was in fact low and safely below the recommended guidelines values for DBAN (70 µg/L), and DCAN (20 µg/L) (WHO 2011b) during both disinfection processes.

All the above observations confirmed that the final disinfection with chloramines is an effective way to control the formation of regulated and unregulated DBPs in distribution systems and meet the regulatory requirements.

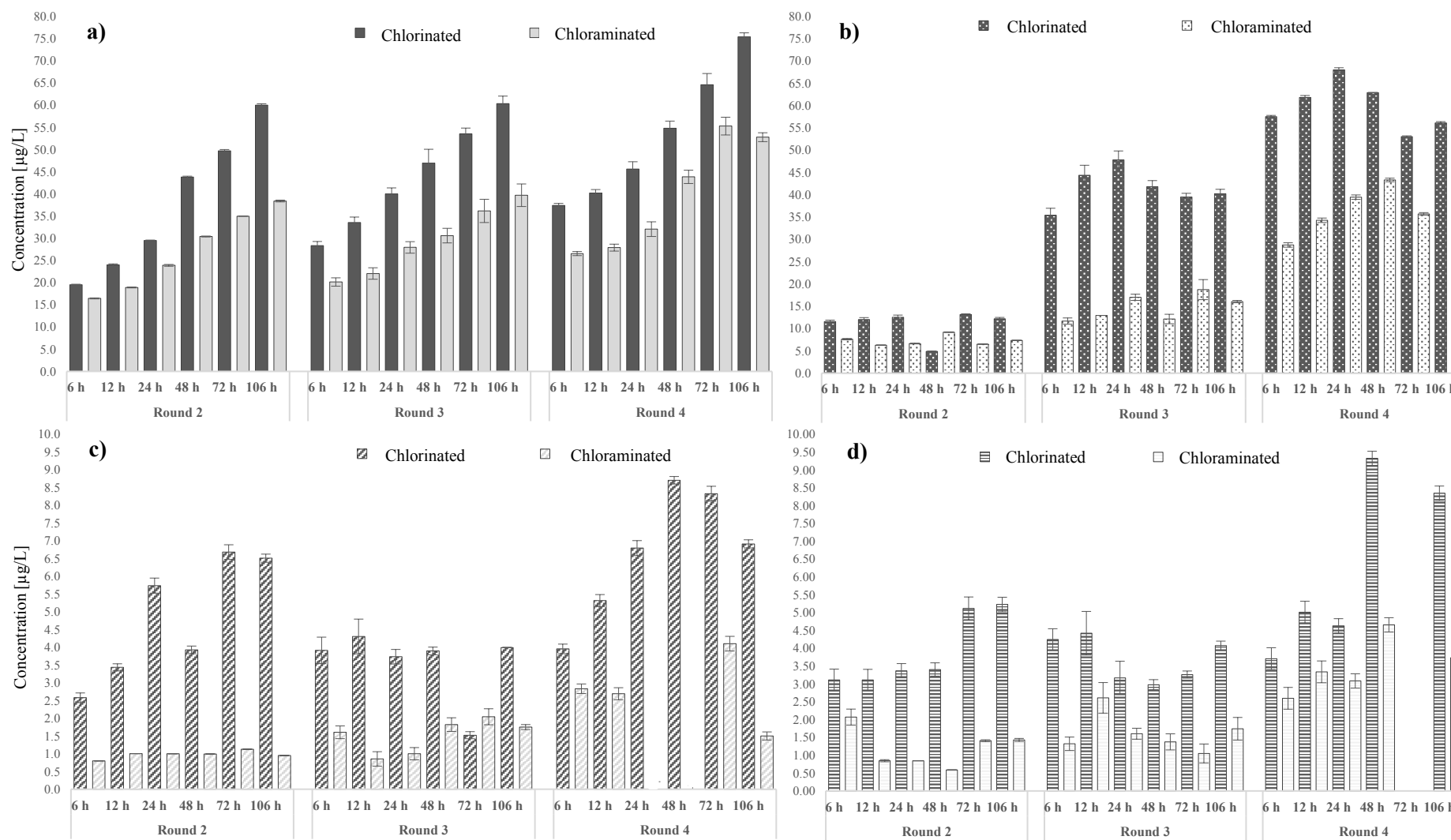


**Figure 5.25:** Comparison of total DBP yields in chlorination and chloramination of *a)* THMs, *b)* HAAs, *c)* HANs and *d)* HACams in WTW A.

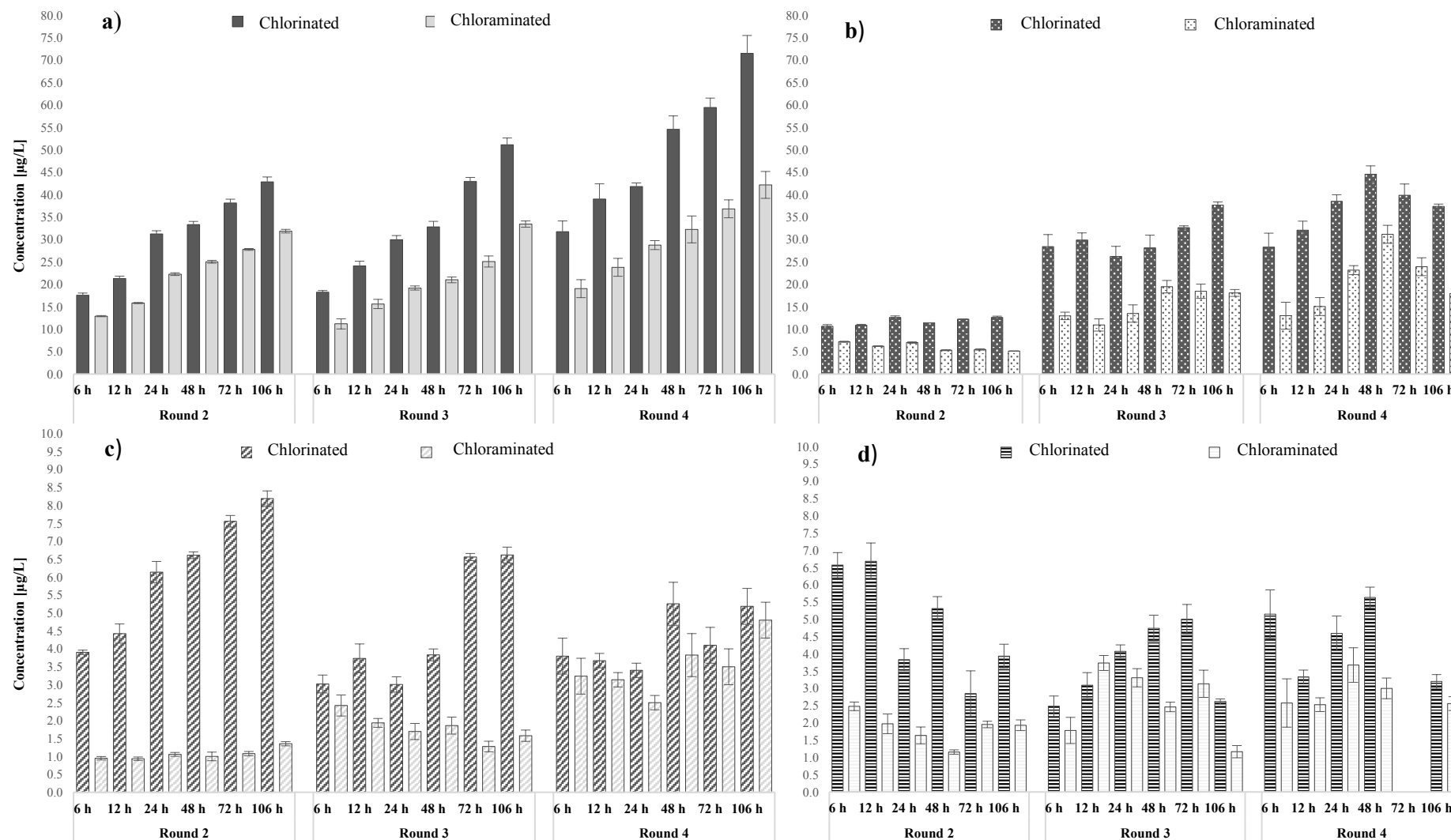


**Figure 5.26:** Comparison of total DBP yields in chlorination and chloramination of *a)* THMs, *b)* HAAs, *c)* HANs and *d)* HACams in **WTW B**.

### 5.3.2 Switching from chloramines to chlorine

Even though switching from chloramines to chlorine is not a usual anticipating practice by water utilities, it was decided that the generation of DBP data from such an event would provide a more thorough understanding of minimisation strategies. Therefore, commonly chloraminated systems (*WTW C & D*) were chlorinated to further understand the advantages and/or disadvantages of applying chloramines and underline what would be expected if chlorine was applied to overcome emergency situations; bacterial resistance, lead exposure (Tibbetts 2007; Miranda et al. 2007).

In more detail, switching from *chloramines to chlorine* in WTW C, resulted in median **increases** of 31% in THM, in 48% in HAAs, 66% in HANs and 42% in HAcAms. Whereas, switching from chloramines to chlorine in WTW D, reported median **increases** of 24% in THM, 12% in HAAs, 44% in HANs and 42% in HAcAms. Contrary to the previous systems (A and B) that were chloraminated, these presented significantly different increase trends when chlorinated, especially in the case of HAAs, and to a lesser extent in THMs.

When chloramines were usually applied as the final disinfectant, **THMs** concentrations in WTW C varied between 17-38.2 µg/L from 6 to 106 hours (*median: 26 µg/L*) during the selected sampling rounds, whereas, when chlorination was applied by SDS tests, THM concentration varied between 24.5-48.4 µg/L from 6 to 106 hours (*median: 35.4 µg/L*) for the same sampling rounds. Likewise, when chloramines were usually applied as the final disinfectant, THMs concentrations in WTW D ranged between 11.7-35.2 µg/L from 6 to 106 hours (*median: 22.2 µg/L*) during sampling *Round 3*, whereas, when chlorination was applied, THM concentration ranged between 15.3-45.3 µg/L (*median: 31.4 µg/L*) for the same water age range. This suggested that the current disinfection practice, in WTW C and D, is efficiently controlling the formation of regulated DBPs. Yet the application of chlorine in systems C and D, regardless of the increase in THMs yields, showed that was not enough to cause exceedance in the water utility's internal limit of 50 µg/L. It is noteworthy that during this disinfectant alteration experiment the rate by which THMs were increased in distribution between 6 and 106 hours remained the same amongst the two disinfection practices in both selected systems. More specifically, in WTW C, THMs presented an increase of 48% and 53% during chlorination and chloramination, respectively, whereas in WTW D this increase was of a level of 66.2% and 66.8% during chlorination and chloramination, respectively. This observation indicated that the previous comment in Chapter 5.3.1, where switching to chloramines essentially also restricted the rate by which THMs generated, was valid only for pre-formed chloramines and not for in line chloramines, applied

in this experiment for WTW C and D. However, since water utilities are typically applying *in line* chloramination (chlorine prior to ammonia) to achieve the required CT for microbial inactivation should expect the same formation rates within their networks during both free chlorination and chloramination. Similarly, to the previous opposite disinfectant alteration experiment, the increase percentages with the implementation of free chlorine did not present any significant spatial and temporal variations between the sampling events, therefore extreme increases are not expected to occur under normal operational conditions on a seasonal basis.

Moreover, the percentage of incorporated bromide in THMs was confirmed, once more through this analysis, to be similar during both chlorination (*median: 90% in C and 70% in D*) and chloramination (*median: 88% in C and 71.5% in D*) in the selected water matrices, regardless of the occurrence differences. Concerning the response of **HAAs**, a similar trend was reported as observed for THMs in that concentrations in chloraminated waters were lower when compared to those using chlorine. Nevertheless, the increase percentage in total HAAs levels by switching to chlorine from chloramines was more pronounced (*median increase: 48%*) than for THMs (*median increase: 31%*), but very similar to the opposite pattern observed by switching to chloramines from chlorine (*median reduction: 47%*) only at WTW C. The benefits of applying chloramines instead of chlorine at WTW D to control HAAs formation was less noticeable (*median reduction: 12%*), which was possibly more related to the pretreatment type of slow sand filtration rather than the selection of disinfectant. In any case, median HAAs levels during chloramination were 28.5 µg/L and 21.3 µg/L in WTW C and D, respectively, whereas during chlorination under the same spatial and temporal conditions were 35.4 µg/L and 33.9 µg/L. The temporal distribution of HAAs indicated that concentrations did not have any specific increase or decrease pattern between 6 and 106 hours during the two disinfection practices, since total HAAs were found to both increase and decrease with time (*Figure 5.27-b and 5.28-b*). However, it was surprising that in the disinfectant alteration experiment of WTW C during Round 2, the levels of total HAAs were reported to be slightly higher in chloramination than those in chlorination in two water ages; 48 and 72 hours (*Figure 5.27-b*). Even though initially and until 24 hours, HAAs occurrence in the chlorinated and chloraminated samples of WTW C followed the same degradation pattern, after 24 hours and until 48 hours HAAs in the chloraminated samples increased, while those in chlorinated continued to decrease. Unfortunately, the investigation on the differentiating factors that may have influenced the elevated occurrence of HAAs in chloraminated systems during the two water ages, such as pH, TOC, residual, were not confirmed by the detailed database.

Even if the current application of chloramines in system C has kept HAAs levels below the suggested internal limit of 40 µg/L, the same cannot be safely said for WTW D. Nonetheless, any switching to chlorine will increase significantly the risk of exceeding not only the internal marker (<40 µg/L) but also the regulatory limit currently effective in the US (<60 µg/L), since yields of 62 µg/L were also reported.

Furthermore, regardless of the speciation patterns reported in literature concerning the dominance of di-HAAs and the low tri-HAAs levels during chloramination (Diehl et al. 2000; Krasner et al. 2008), these are not necessarily confirmed in his study. Dihalogenated HAAs were dominant not only during chloramination but also during chlorination, only in waters from WTW C. At WTW D, trihalogenated species were the dominant species during both disinfection processes and water ages. Since Reckhow et al. (1990) have suggested that di-HAAs and tri-HAAs follow different mechanistic pathways, and thus not necessarily share the same precursors, the above deviation may be due to the poor efficiency of slow sand filtration, currently applied in WTW D, to even remove tri-HAAs precursors, characterised as more hydrophobic than those of di-HAAs (Liang and Singer 2003). Finally, the percentage of bromine containing HAAs species was similar or higher in chlorinated samples, with calculated median BIF of 0.4 and 0.2, during chlorination and chloramination, respectively. This observation is not in agreement with the previous finding on the increased bromide incorporation during chloramines implementation (Chapter 5.3.1), which, however, may be valid only for pre-formed chloramines and not for in-line chloramines.

Similarly to HAAs, the effect in switching from chloramines to chlorine was significant for **HANs** (Figures 5.27-c and 5.28-c) and **HAcAms** (Figures 5.27-d and 5.28-d), since all N-DBP levels increased in both selected systems during all water ages and sampling events that this comparison took place. In more detail, in WTW C the median concentration of HANs changed from 1.9 µg/L in chloraminated samples to 5.5 µg/L when using chlorine, whereas median concentration of HAcAms changed from 5.1 µg/L to 8.2 µg/L. The occurrence of HAcAms in the currently chloraminated WTW C was the highest reported in all selected systems, and was higher even from those currently applying chlorine (A and B). However, when chlorine was implemented in the water matrix of WTW C the risk of generating HAcAms increased by 42% (*median*), which supported further the argument that chloramines (pre-formed and in-line) do not form more HANs or HAcAms. The maximum of total HAcAm concentration during chlorination was above 10 µg/L, and was reported even during low to medium water ages (12, 24 hours), namely two times higher than the median concentration reported during chloramination. In addition, the fact that the median minimisation percentage of HANs (64%) and HAcAms (50%) when switching to *pre-formed* chloramines,

previously observed in Chapter 5.3.1, did not present a significant deviation to the minimisation percentage when using in-line chloramines, 59% and 42% for HANs and HAcAms, respectively, indicated that the chloramination mode had a minimal impact on the research conclusions. Likewise, in WTW D the median concentration of HANs changed from 1.9 µg/L in chloraminated samples to 3.4 µg/L when using free chlorine, whereas median concentration of HAcAms changed from 4.1 µg/L to 6.9 µg/L. Even though with the use of pre-formed chloramines the dominant species of HANs were reported below the detection limits, the same was not observed with in-line chloramines. In fact, the predominant HANs species in WTW C during chlorination, namely DBAN and DCAN, decreased in concentration but remained the predominant species during in-line chloramination, as did TCAN and DCAN in WTW D. As mentioned before, the impact of chloramination on HANs and HAcAms speciation remains unclear. The results of this study, though, suggested that speciation shifted towards dihalogenated HANs and HAcAms during chloramination and to a lesser extent during chlorination, whereas TCAN and tri-HAcAms generally occurred in low levels during both disinfection practices. This pattern was similar to the pattern observed in the speciation shifting in HAAs (Diehl et al. 2000; Krasner et al. 2008), which suggested that these groups may share similar precursors. Concerning the level of bromination, during chloramination it was reduced in HANs, whereas in HAcAms was generally equal between the two disinfection practices. In more detail, bromine containing HANs represented approx. 55% of total HANs yields during chlorination, whereas represented 33% during in-line chloramination. The same comparison from Chapter 5.3.1 indicated that the implementation of pre-formed chloramines would reduce further the bromination levels of HANs. In the case of HAcAms, bromine-containing HAcAms species represented a median of 80% and 83%, during chlorination and chloramination, respectively. When the bromide incorporation factors were compared, the above findings are further confirmed since median BIF in total HANs was 0.4 and 0.3 in chlorination and chloramination, respectively, while the same factor was equal (0.4) for HAcAms during both disinfection methods. The detailed tables of calculated BIF values organised by treatment plant, DBP group, water ages and disinfection methods are summarised in *Appendix D. Summary of Bromine Incorporation Factors*.

In any case, the results indicated that regardless of the disinfection method application, the occurrence of HANs in the monitored systems was safely below the recommended guidelines values for DBAN (70 µg/L), and DCAN (20 µg/L) (WHO 2011b).

The findings of this chapter indicated that the implementation of chloramines in WTW C and D provided the optimal results in the formation of the target regulated and unregulated DBPs, and therefore the collaborative water utility is advised to maintain the current disinfection practice to avoid increased levels of the regulated THMs.

As mentioned above, chloramination in systems A and B was applied with pre-formed chloramines whereas in C and D with in-line, therefore a significant experimental deviation was expected in the calculated percentages, especially in the case of THMs and HAAs. However, from the decrease and increase percentages of DBPs calculated it was observed that this experimental difference was not crucial, since these percentages were very similar regardless of the chloramination mode, especially in the systems that had similar pre-treatment methods. In all these three systems (*A, B and C WTW*) the formation of THMs, HAAs, HANs and HAcAms presented similar optimization trends with the use of chloramines as a final disinfectant. This indicated that the SDS tests with pre-formed chloramines predicted the formation of DBPs in distribution to a high extent, without necessarily being a conservative scenario. Nevertheless, it has to be noted that in WTW D, the disadvantages of applying chlorine compared with in-line chloramines were less profound in the minimisation of THMs and HAAs. This observation though may not be necessarily linked with the chloramination mode but with the relative ineffectiveness of slow sand filtration to remove DBP precursors during water treatment in this system.

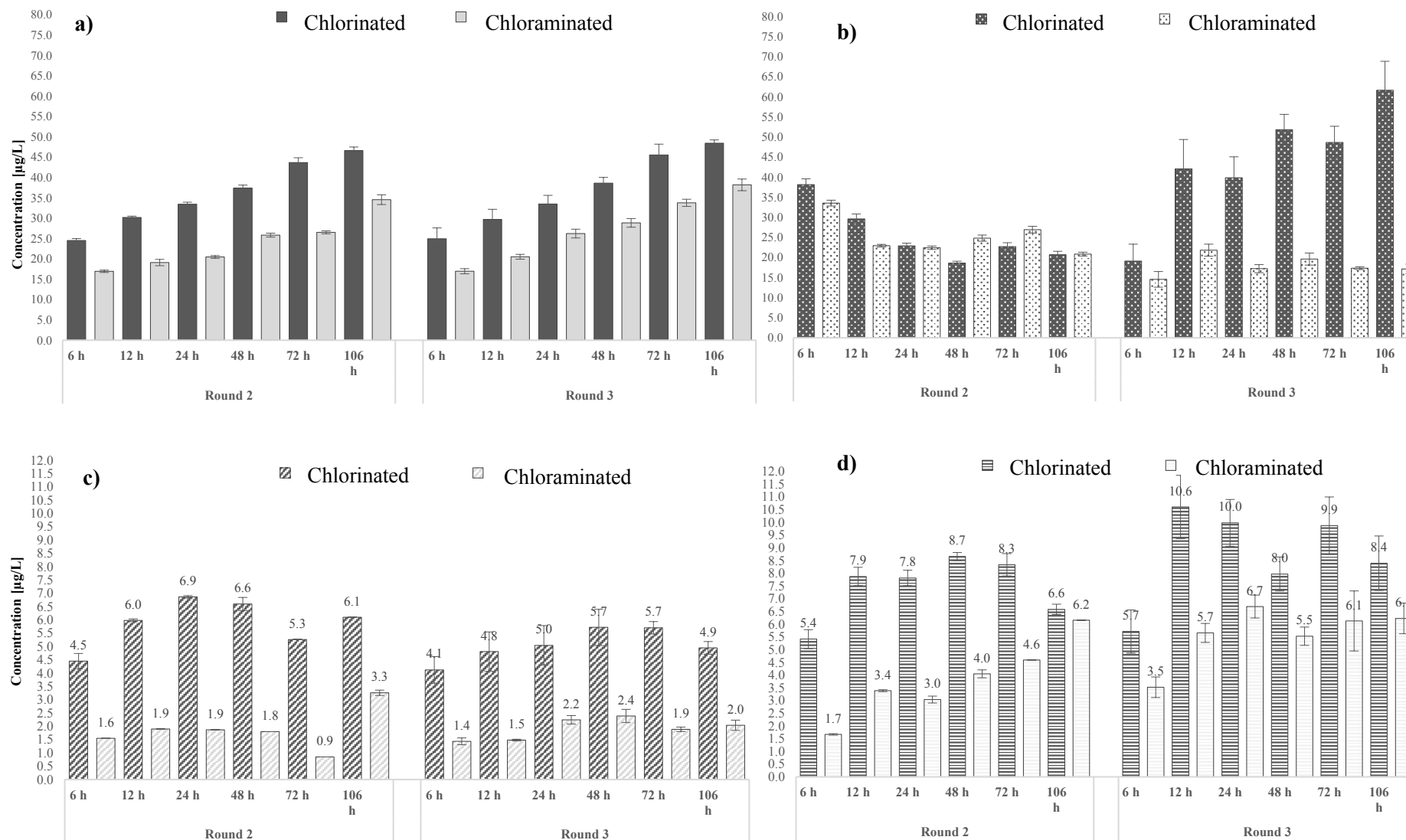


**Figure 5.27:** Comparison of total DBP yields in chlorination and chloramination of **a)** THMs, **b)** HAAs, **c)** HANs and **d)** HAcAms in WTW C.

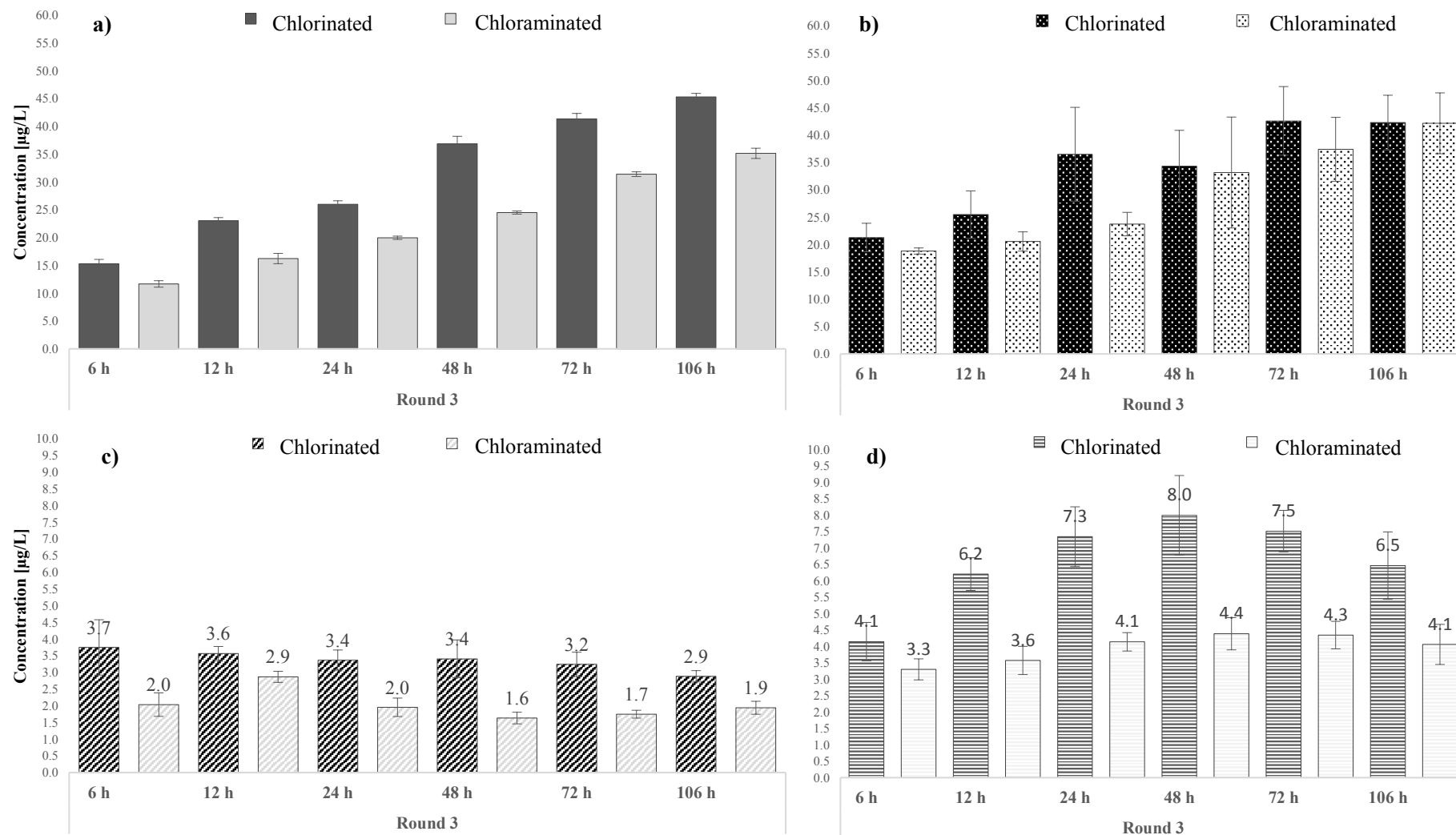


**Figure 5.28:** Comparison of total DBP yields in chlorination and chloramination of **a)** THMs, **b)** HAAs, **c)** HANs and **d)** HAcAms in WTW D.

## 5.4 Investigation of amides as N-DBP precursors

The above findings from the annual monitoring of DBP fate in distribution systems, via the collection of actual distribution samples and the implementation of SDS tests, indicated that multiple factors influence the formation of regulated and unregulated DBPs in drinking water. Even though a preliminary understanding of the factors that influenced the formation and degradation of N-DBPs in distribution systems was possible, the relative importance of these remains unclear, since water samples should be considered primarily as mixes. As previously mentioned in the literature, the quantity and quality of the natural organic matter found in water matrices is an important DBP formation factor that determines not only the levels but also the type of DBPs formed. Following the publication of Huang et al. (2012), who suggested the independent formation of HAcAms from organic precursors instead of HANs hydrolysis products, several studies have investigated the nitrogenous and non-nitrogenous organic moieties as N-DBPs precursors (Bond et al. 2014; Chu et al. 2015; Nihemaiti et al. 2016; Le Roux et al. 2016). This is the first time that amides are directly oxidized, by free chlorine and chloramines, to examine their potential of functioning primarily as HAcAms precursors, and further as HANs, HAAs and THMs precursors.

This study investigated the relative effect of six model amide precursor compounds to act as organic precursors for N-DBPs, upon chlorination and chloramination, under a range of water quality conditions (pH, bromide dose and water age). The amide model compounds that were considered are summarised in Table 4.4 and a detailed analysis upon their selection can be found in Chapter 4.4.1. The DBPs quantified in this study were 8 haloacetamides (HAcAms) and 5 haloacetonitriles (HANs), capturing the chlorinated and brominated compounds; trihalomethanes (THMs) and haloacetic acids (HAAs) were also included in the analysis to facilitate correlations.

An improved understanding regarding the tendency of amides to form HAcAms and HANs in drinking water will highlight their relative importance compared to other DBP precursors, and the implications for N-DBP minimisation strategies in water treatment practice. Preliminary experiments (*screening phase*) were conducted at pH 8 (10 mM phosphate buffer) for 24 hours in the absence of bromide to investigate the formation yields of chlorinated species of N-DBPs, during chlorination and chloramination. Whereas, the *detailed phase* incorporated supplementary experiments in both pH 7 and 8, for 4 and 24 hours, with the presence of bromide during chlorination and chloramination.

### 5.4.1 Results of screening phase

During the screening phase of the study, HAcAms (DCAcAm, TCAcAm) and HANs (DCAN, TCAN) yields, as well as HAAs (MCAA, DCAA, TCAA) and chloroform yields were observed from all selected amides during both chlorination and chloramination (**Figures 5.30-5.32**). In general, total HAcAm yields from chlorination were lower than those of total HANs, while in chloramination total HAcAm yields were higher than those of total HANs; with exceptions for HAcAms formation from acetamide,  $\beta$ -alaninamide and hydroxybenzamide. These results agree with previous model precursor studies by Chu et al. (2016) and Huang et al. (2017) for the same retention time (24 hours), with regards to which N-DBP species are favoured during each disinfection application. Namely, upon chlorination of a solution containing NOM, Huang et al. (2012) indicated that the sum of HANs and HAcAms was respectively, 67 nM and 10 nM while upon chloramination was 12 nM and 20 nM. In this study, of note, amide compounds formed relatively limited TCAN (only 2/6 amides) and undetectable levels of DCAN during chloramination, compared to the formation of their relative HAcAm species, DCAcAm and TCAcAm. In particular, acetoacetamide formed significantly more DCAcAm (0.04 % M/M) and TCAcAm (0.40% M/M), relative to TCAN (0.02% M/M) and DCAN (undetectable). The above gave an initial indication that DCAcAm and TCAcAm yields were not solely due to the hydrolysis of DCAN and TCAN, which has been the most studied pathway (Reckhow et al. 2001; Krasner et al. 2006; Chu et al. 2010) and that it could also form independently. In addition, the results of the actual and simulated distribution monitoring, already discussed (Chapter 5.1-5.2) investigated further the temporal relationship between these two species, and highlighted that the gradual decrease of HANs species was not always associated with simultaneous HAcAms increase. Moreover, the exceptions observed highlighted the importance of precursor's structure in relation with chemical functionality, as reactions of chlorine are possibly faster than those of chloramines, since free chlorine reacts predominantly by transferring a Cl [+1], whereas chloramines form intermediates (Chuang et al. 2015). So, the reason why some compounds are reported to form higher HAcAms yields in chlorination is either due to their structural advantage upon free chlorination, to the different formation pathways or to the slower formation pathway from chloramines.

The molecular structure character of amides presented a significant influence in the formation of HAcAms among the six amides. Indeed, acetoacetamide presented the highest formation yield of HAcAms during both chlorination and chloramination, 0.22% ( $\pm 0.01$ ) M/M and 0.44% ( $\pm 0.07$ ) M/M, respectively. Even though acetamide has a simpler but similar structure to acetoacetamide, formed significantly less HAcAms.

This is possible since acetoacetamide contains a  $\beta$ -dicarbonyl group that has been reported to be a very reactive structural moiety with halogens (Dickenson et al. 2008). However, during chlorination acetamide presented the second highest yield ( $0.09\% \pm 0.02$  M/M), as its conversion to a haloacetamide is a rapid one-step reaction in comparison with the remaining four amides. Interestingly, the aromatic nature of hydroxybenzamide, did not favour HAcAm formation as expected during both disinfection processes; literature suggests that a ring-cleavage reaction is triggered when the aromatic ring is activated by the hydroxyl group encouraging chlorine electrophilic substitution (Hureiki et al. 1994; Chu et al. 2010; Nihemaiti et al. 2016). However, this was not observed from the results of the screening phase, due to the possible advantage of aliphatic moieties including beta dicarbonyl and electron donating groups on the  $\beta$ -carbon (e.g.  $-\text{NH}_2$ ) in comparison with the aromatic moiety (Dickenson et al. 2008). As shown in **Table 5.10**, during chlorination, the most abundant HAcAm species was DCaAcAm with reported yields ranging from 0.02-0.014%, followed by TCaAcAm that was only identified in three of the selected amides. The above is in agreement with Chu et al. (2013) study on HAcAm precursors in natural waters, where DCaAcAm is reported to generate more easily than TCaAcAm during chlorination.

During chloramination, the increasing number of carbon atoms of the aliphatic amides facilitated the formation of HAcAms (increasing chloramine doses, linked to fixed  $\text{Cl}_2/\text{C}=1:1$ ). On the other hand, the aromatic amide (hydroxybenzamide), that has the highest number of carbons, did not form DCaAcAm and formed very low TCaAcAm. This is possibly observed for two reasons; chloramine cannot trigger the rapid opening of the benzene ring (Chu et al. 2016) or the HAcAms previously formed at lower retention times, regardless of their amount were prone to hydrolyse in a faster rate. During chloramination, DCaAcAm yields reported were significantly similar to a previous study on nitrogenous amino acids by Le Roux et al. (2016), but higher than those reported in a study on non-nitrogenous organic acids (Chu et al. 2016). Even though tracing the origin of nitrogen in N-DBPs was not in the scope of this work, the above indicates that the predominant mechanism in our case is the incorporation of nitrogen from the nitrogen-containing amides into HAcAms and not the incorporation of inorganic nitrogen from the chloramines.

**Table 5.10:** N-DBPs yields from model amide compounds during chlorination and chloramination.

|                      | Molar yield [%] (SD) |             |             |             |                |             |      |             |
|----------------------|----------------------|-------------|-------------|-------------|----------------|-------------|------|-------------|
|                      | Chlorination         |             |             |             | Chloramination |             |      |             |
|                      | DCAcAm               | TCAcAm      | DCAN        | TCAN        | DCAcAm         | TCAcAm      | DCAN | TCAN        |
| Acetamide            | 0.08 (0.02)          | 0.01 (0.00) | 0.02 (0.01) | 0.07 (0.01) | 0.02 (0.01)    | -           | -    | -           |
| Acetoacetamide       | 0.14 (0.00)          | 0.08 (0.01) | 0.03 (0.00) | 0.06 (0.01) | 0.04 (0.01)    | 0.40 (0.06) | -    | 0.02 (0.01) |
| Polyacrylamide       | 0.04 (0.01)          | -           | 0.03 (0.00) | 0.05 (0.00) | 0.04 (0.01)    | 0.03 (0.00) | -    | -           |
| Acrylamide           | 0.04 (0.00)          | -           | 0.03 (0.00) | 0.09 (0.02) | 0.15 (0.01)    | 0.01 (0.00) | -    | -           |
| $\beta$ -Alaninamide | 0.06 (0.01)          | -           | 0.03 (0.00) | 0.05 (0.01) | 0.02 (0.00)    | 0.02 (0.00) | -    | -           |
| Hydroxybenzamide     | 0.02 (0.00)          | 0.04 (0.00) | -           | 0.14 (0.01) | -              | 0.01 (0.00) | -    | 0.17 (0.01) |

Note: The use of (-) symbol indicates the individual DBP species that were not detected in the samples.

The different observations in HAcAms yields during free chlorination and chloramination designates that different isolates might have distinctive HAcAms pathways and/or a different formation rate, as shown in

**Figure 5.29.**

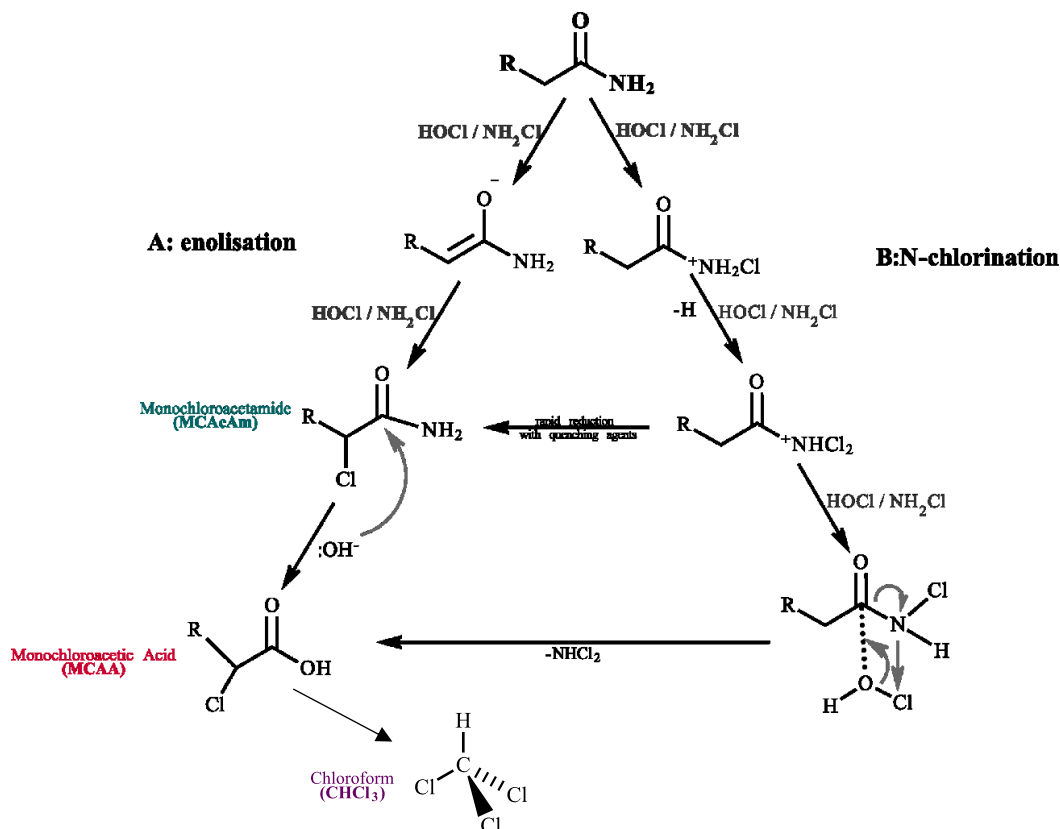


**Figure 5.29:** Proposed formation pathway of HAcAms and other by-products from chlorination of an amide (adapted from Clayden et al. 2001; Nihemaiti et al. 2016; Yu and Reckhow 2017).

Concerning the HANs yields, their formation was not expected, since there is not a known reaction pathway from an amide to form a haloacetonitrile. During chlorination, HANs yields (DCAN and TCAN) were reported from all amides, whereas in chloramination, TCAN was the only species detected for acetoacetamide and hydroxybenzamide. It is noteworthy, that during chlorination, HANs formation was low and did not vary significantly with the changes in molecular structure of amides, something that indicated experimental interferences. Therefore, several scenarios have been further examined to understand whether any unintended reactions or reagent interference occurred during the experiments. The scenario of amides hydrolysis during the experiments was rejected, as it requires strong acidic or alkaline conditions under high temperature (Clayden et al. 2001). Furthermore, although the quenching agents selected in this study have been previously studied with regards to HAcAm and HAN stability (Liew et al. 2012; Kristiana et al. 2014), the possibility of these acting as reducing agents should be further investigated by simultaneous monitoring of N-DBP preservation. Finally, the instability of monochloramine in water may have introduced intermediate amines in the samples at some point, as literature suggests, through its degradation to nitric and nitrous acid (Diyamandoglu 1994). Unfortunately, the above interference would not have been able to be detected from the analysis of reagent blanks, as the quality control samples were quenched in lower retention time than the actual samples.

Even if these assumptions are valid for the majority of the selected amides, the similar but high TCAN yields from hydroxybenzamide during both chlorination and chloramination ( $0.14\% \pm 0.001$  M/M and  $0.17\% \pm 0.00$  M/M, respectively), showed that the impact of its structure should not be disregarded. Hydroxybenzamide consists of an aromatic ring that contains a strong activating substituent (-OH), so there is a chance that multiple substitution sites are being created by the same molecule. Subsequently, possibly the amide group reacts separately from the phenol group that via incorporation of inorganic nitrogen, found in the quenching agent in chlorination and monochloramine in chloramination, generated HANs.

Concerning the rest of the DBPs identified in the amide samples; in chlorination, haloacetic acids presented statistically significantly higher yields than HAcAms, HANs and chloroform. The maximum yield reported was identified in the samples containing *polyacrylamide* ( $0.78\% \pm 0.09$ ) followed by those with *acetoacetamide* ( $0.60\% \pm 0.07$ ). This indicates that after a retention time of 24 hours that the majority of HAcAms generated have hydrolysed to their relative haloacetic acids. However, the possibility of an unknown alternative pathway should also be considered. Indeed, from the speciation of the HAcAms and HAAs, it is observed that DCAA yields follow a similar formation rate from their relative DCACAm yields

for the five selected amides. The only amide that does not follow this pattern is hydroxybenzamide, possibly because of the low DCAcAm formation rate previously mentioned and the subsequent slower transformation to DCAA in 24 hours. It is noteworthy though, that some of the amides that did not report TCACAm yields (*polyacrylamide*, *acrylamide* and  *$\beta$ -alaninamide*), reported high TCAA yields  $0.38\% \pm 0.06$  M/M,  $0.15\% \pm 0.02$  M/M,  $0.23\% \pm 0.07$  M/M, respectively, even higher than those of DCAA. It is known that trihalo-substituted compounds are more susceptible to hydrolysis (Glezer et al. 1999), especially under basic conditions, so a complete transformation of the TCACAm to TCAA may have happened during lower retention times. Also, apart from the hydrolysis scenario, the high yields of TCAA may be linked to the fact that TCAA formation proceeds through the further halogenation of the common dihalogenated intermediate, initially introduced by Cowman and Singer (1996), so there might be two collaborative formation mechanisms; TCACAm hydrolysis or DCAA halogenation. Once more, hydroxybenzamide samples are an exception, having formed TCACAm but no TCAA after 24 hours of incubation. Also, as illustrated in **Figures 5.31** and **5.32**, a significant amount of MCAA was yielded upon chlorination of acetoacetamide and polyacrylamide, similar to DCAA yields, whereas upon chloramination MCAA yield were reported in all amide samples in a lower amount than chlorination.

During chloramination, the HAAs yields reported were significantly lower than those reported during chlorination, with reduction ranging 42-75%. The most prominent HAAs species in chloramination was TCAA and MCAA, as DCAA yields were not identified at all. This is possibly due to the low stability and faster degradation of TCACAm to form TCAA in comparison with the dichloro-compounds. So, there is a possibility that the DCAcAm was either highly stable under the current conditions or had not hydrolysed, yet at the selected retention time, to form DCAA. However, the absence of DCAA yields and the higher yields of TCAA than TCACAm, designated that apart from HAcAms hydrolysis, chloramination favoured further halogenation of the supposed dihalogenated intermediate instead of oxidation or hydrolysis to form DCAA.

Since the screening phase did not involve any bromide addition in the amide samples, the only trihalomethane that was reported was chloroform. Chloroform yields were reported only during chlorination of the six amides, whereas during chloramination was either not formed or was below the detection limit. The most reactive amide was  $\beta$ -alaninamide with a yield of  $0.28\% \pm 0.02$  M/M, followed by acetoacetamide with a yield of  $0.16\% \pm 0.00$  M/M. The higher yield in  $\beta$ -alaninamide samples is possibly linked to the fact that includes beta carbonyl activated by  $-\text{NH}_2$  (electron donating group) (Dickenson et al.

2008). The presence of chloroform in varying degrees was explained by two mechanisms (Reckhow et al. 1990); either as hydrolysis product of tri-HAAs, favoured by base-catalysed hydrolysis of the halogenated leaving group (**Fig. 5.29**) or as independent by-product of amide oxidation via a currently unknown pathway.

The results of the screening phase indicated that even amides, which are classified as the least reactive derivatives towards nucleophiles (Clayden et al. 2001), can function as HAcAms, HAAs and chloroform precursors during both chlorination and chloramination.

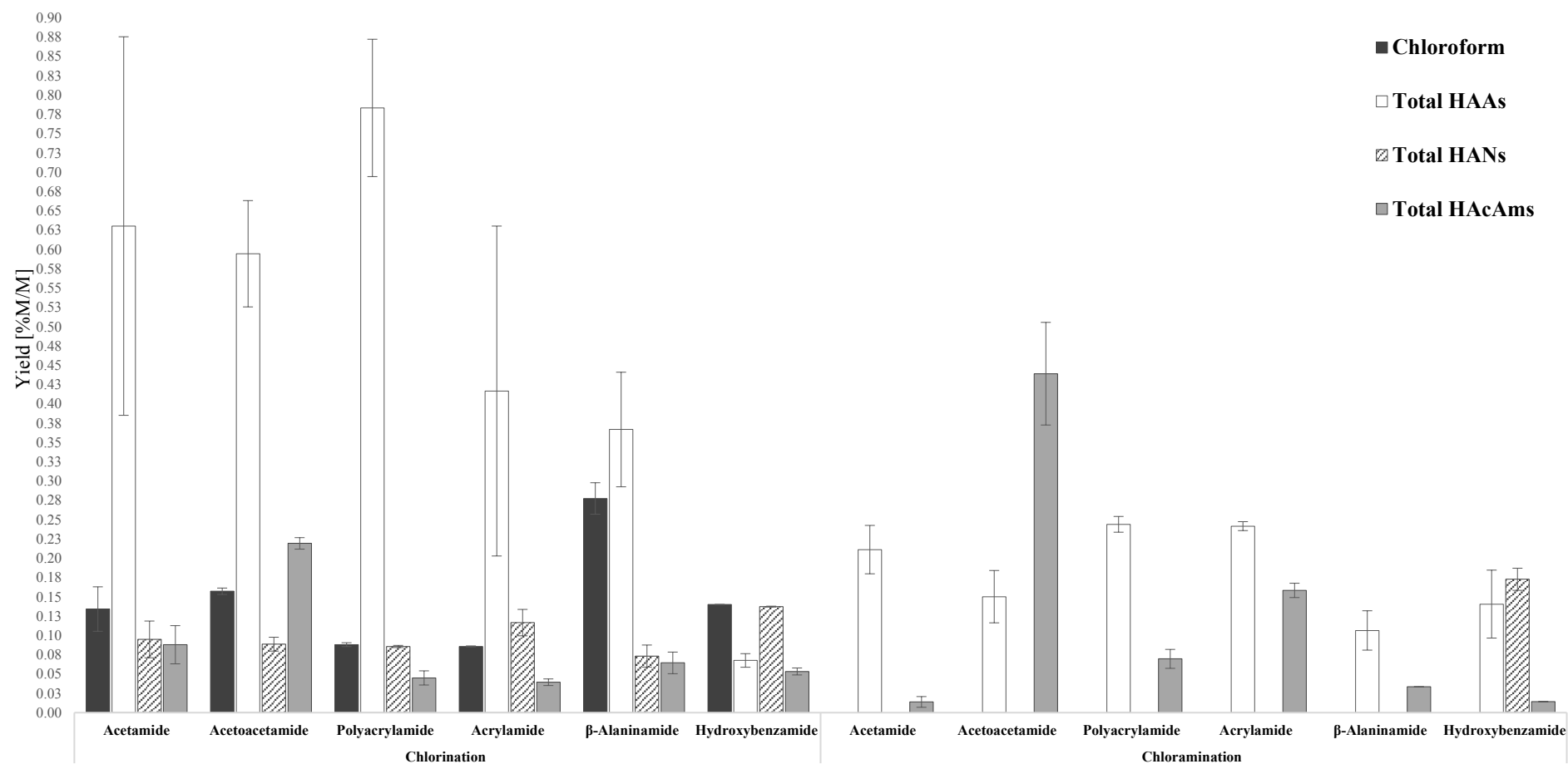


**Figure 5.30:** DBP yields from **chlorination** and **chloramination** at **pH 8** after **24 hours** of retention time. Error bars represent the range of duplicate experiments.

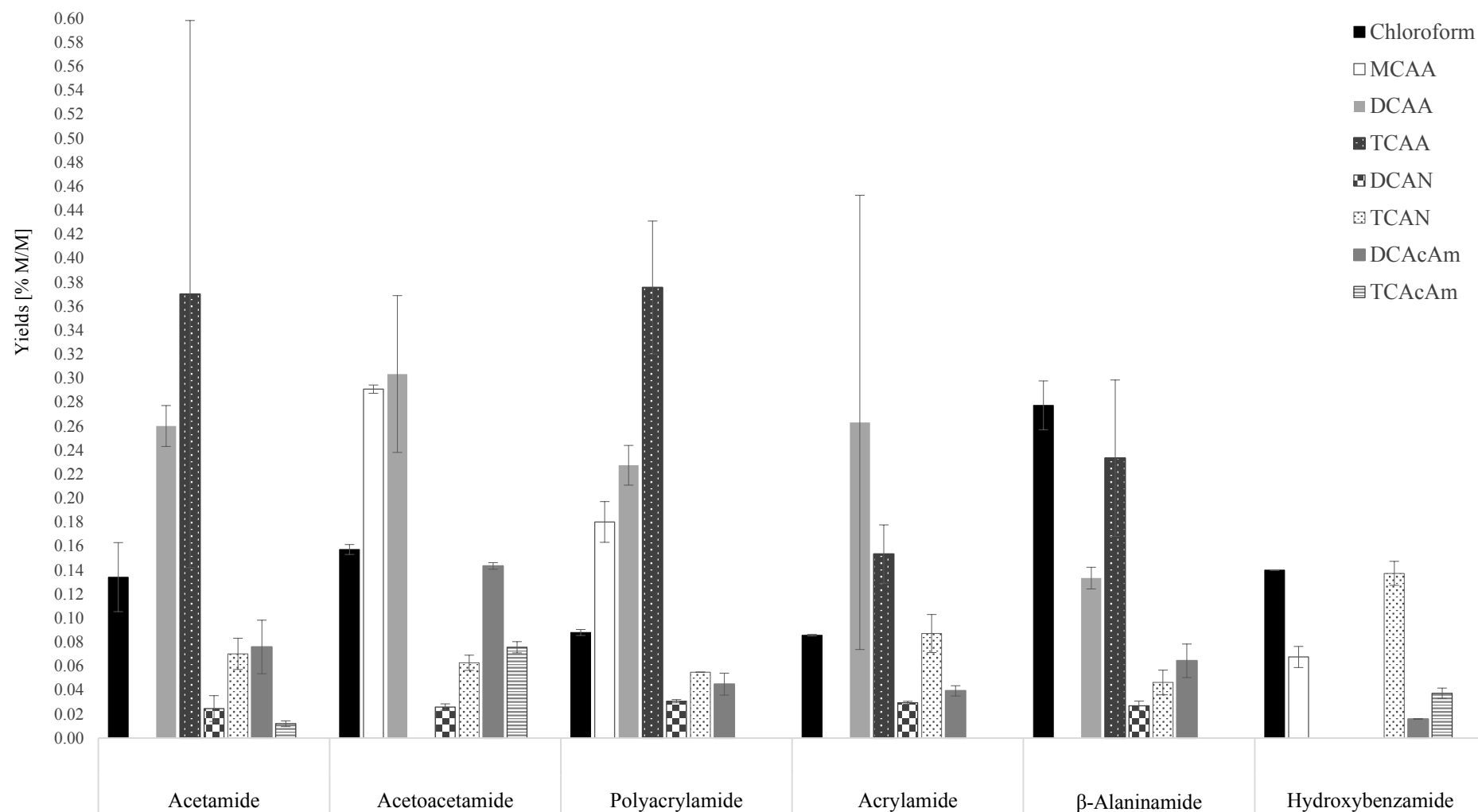


**Figure 5.31:** DBP yields speciation from chlorination at pH 8 after 24 hours of retention time. Error bars represent the range of duplicate experiments.

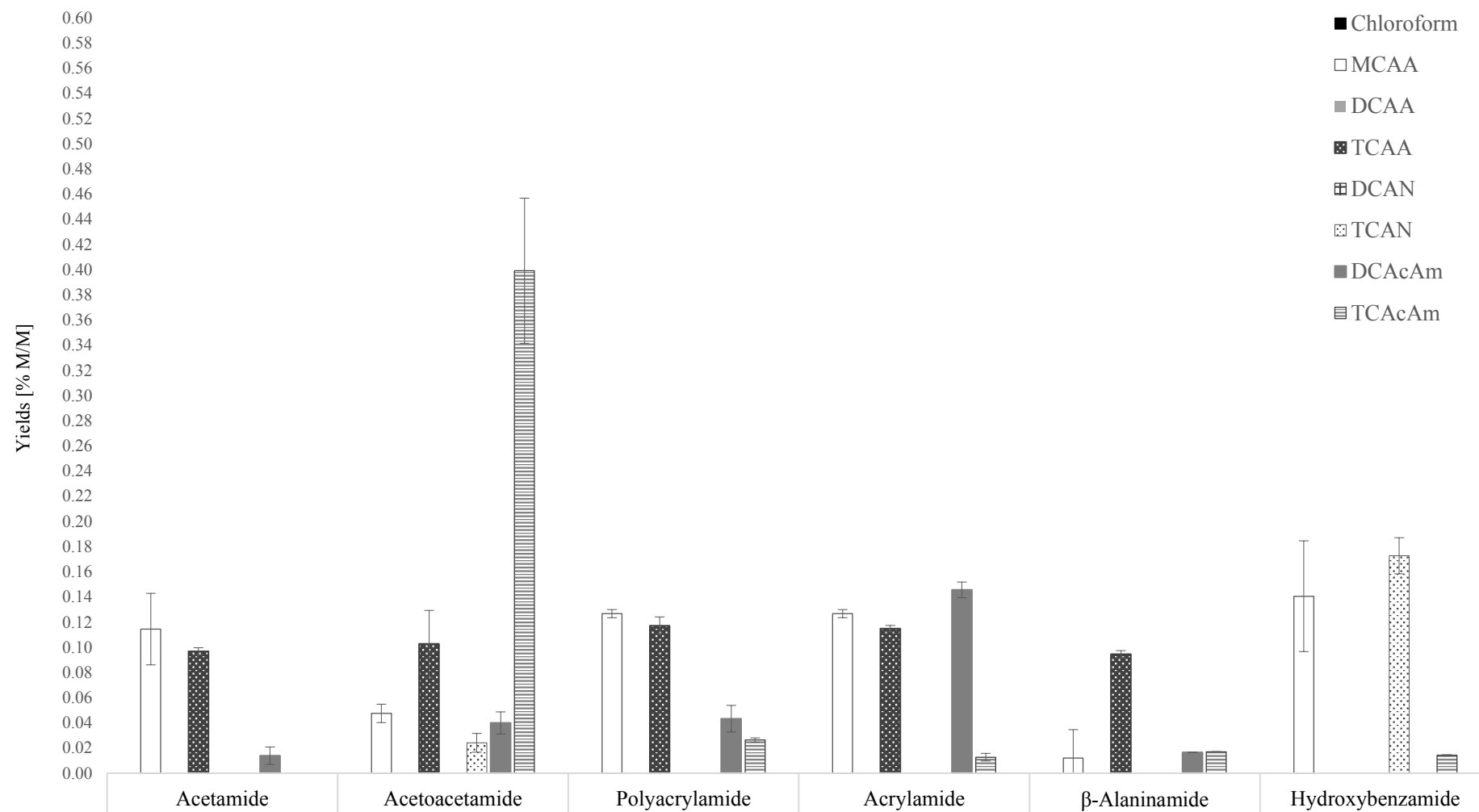


**Figure 5.32:** DBP yields speciation from **chloramination** at **pH 8** after **24 hours** of retention. Error bars represent the range of duplicate experiments.

## 5.4.2 Results of detailed phase

The results of the preliminary tests demonstrated the potential of the six selected amides to generate yields of HAcAms and other disinfection by-products during chlorination and chloramination. However, at the same time highlighted the importance of their structure and raised questions concerning the performance of the same amides under other conditions. Therefore, the above experiments were enriched and repeated under two pH values (pH 7 & 8), two retention times (4 & 24 hours) and bromide dose (0 & 100 µg/L).

### 5.4.2.1 Formation of haloacetamides (HAcAms)

During the detailed phase, HAcAms were identified during both chlorination and chloramination of the amide samples. The most reactive amide that produced the highest total yield of HAcAms during chlorination with the absence of bromide was *β-alaninamide* (1.32% M/M) at pH 7 after 24 hours, followed by hydroxybenzamide that formed significant lower yields (0.45% M/M) at the same pH in lower retention time of 4 hours (**Figure 5.33**).

More specifically, *polyacrylamide* had a stable formation of HAcAms with time in both pH 7 and 8, reporting median yields as high as  $0.064 \pm 0.003$  % M/M at pH 7 and  $0.051 \pm 0.008$  % M/M at pH 8. *Acetamide*, on the other hand, presented similar behaviour with the above, only at pH 8, where the HAcAm yield was equal and stable for both retention times ( $0.088 \pm 0.00$  % M/M). However, it was interesting that for the same amide, in pH 7 the HAcAms formed at 4 hours (molar yield of 0.045% M/M) were not detected after 24 hours. This was due to HAcAms hydrolysis and was related to subsequent increase of HAAs during the same conditions. Decreasing but almost equal HAcAms yields in pH 7 and pH 8 were also observed with *acetoacetamide*, during the retention times of 4 hours (0.26% and 0.22%, respectively) and 24 hours (0.12% and 0.13%, respectively). In the case of *hydroxybenzamide*, different amounts of HAcAms were formed in each pH in 4 hours, which both started to degrade after 24 hours. An interesting observation, though, was the fact that the reduction rate of HAcAms yields was higher in pH 7 than in pH 8. *Acrylamide*, formed zero yields of HAcAms at pH 7, whilst at pH 8 the yield that was initially reported in 4 hours was significantly reduced after the retention time of 24 hours (by 89%). The only case, in which HAcAms yields did not decrease with time, was for *β-alaninamide* samples. This trend is more noteworthy in pH 7 than pH 8, where at a retention time of 4 hours total molar yield is 0.19% M/M which then increases to 1.32% M/M after 24 hours. So, with the exception of *β-alaninamide*, generally HAcAm yields decreased between 4 and 24 hours during both chlorination and chloramination at pH 7 and 8.

When bromide was incorporated the amide samples, under various water quality conditions, the database was more informative. Firstly, the results demonstrated that there was a significant increase in the total HAcAms yield, for all the amides tested, without exception, in both chlorinated and chloraminated samples, with increases ranging between 35-98%. Another observation was that all amides were reported to be evidently more reactive at pH 7 during both retention times during chlorination conditions, whilst during chloramination, amides became more reactive at pH 8 after a retention time of 24 hours. This was observed due to the increased reactivity of each disinfectant at the two-different pH of this study, since chlorine is more reactive at  $\text{pH} \leq 7.5$  and monochloramine at  $\text{pH} \geq 7.5$  (Kirmeyer et al. 2000; Bowman and Mealy 2007).

The most reactive precursor following chlorination of brominated samples was *acetamide* which had a similar total HAcAms yield during both retention times at pH 7 ( $2.17 \pm 0.02\%$  M/M). This was closely followed by *hydroxybenzamide* samples that reached a peak of HAcAms yield of 2.08% M/M at 4 hours and *acrylamide* of 2.03% M/M in 24 hours, again both at pH 7. Acetamide, formed similar total HAcAms yields that remained relatively stable with time during both pH conditions. This applies to hydroxybenzamide in the samples of pH 8, while at pH 7 the HAcAms yields formed in 4 hours were slightly degraded until 24 hours. In samples with *polyacrylamide* and *acetoacetamide*, a slight decrease (*by median 8%*) of HAcAms yield with time was observed in pH 7 but a significant increase was observed in pH 8 (*by median 48%*). On the other hand,  *$\beta$ -alaninamide* behaves in the opposite way; HAcAms yields were increasing in pH 7 (*by 26%*) and decreasing in pH 8 (*by 36%*) with regards to retention time. In the case of acrylamide, increase in HAcAms yields with time was observed in both selected pH.

With the addition of bromide in chloraminated samples, there is a statistically significant decrease in total HAcAms yields, but only at pH 7. The same cannot be said for chloraminated samples in pH 8, where concentrations are very similar or even higher in limited cases. The reason of this observation has not been yet understood, and may be attributable to the combining effect of chloramine chemistry, bromide, organic structures and pH. Yet it is noteworthy that HAcAms formation followed the same pattern in all the amide samples; In pH 7, HAcAms yields are decreasing whereas in pH 8 are increasing with time. During chloramination in brominated samples, the most reactive amides are acetamide in pH 7 after 4 hours and  *$\beta$ -alaninamide* in pH 8 after 24 hours yielding 0.81 and 0.80% M/M, respectively.

Below, **Figure 5.33** illustrates the yields of total HAcAms formed from the amide samples during the various experimental conditions.

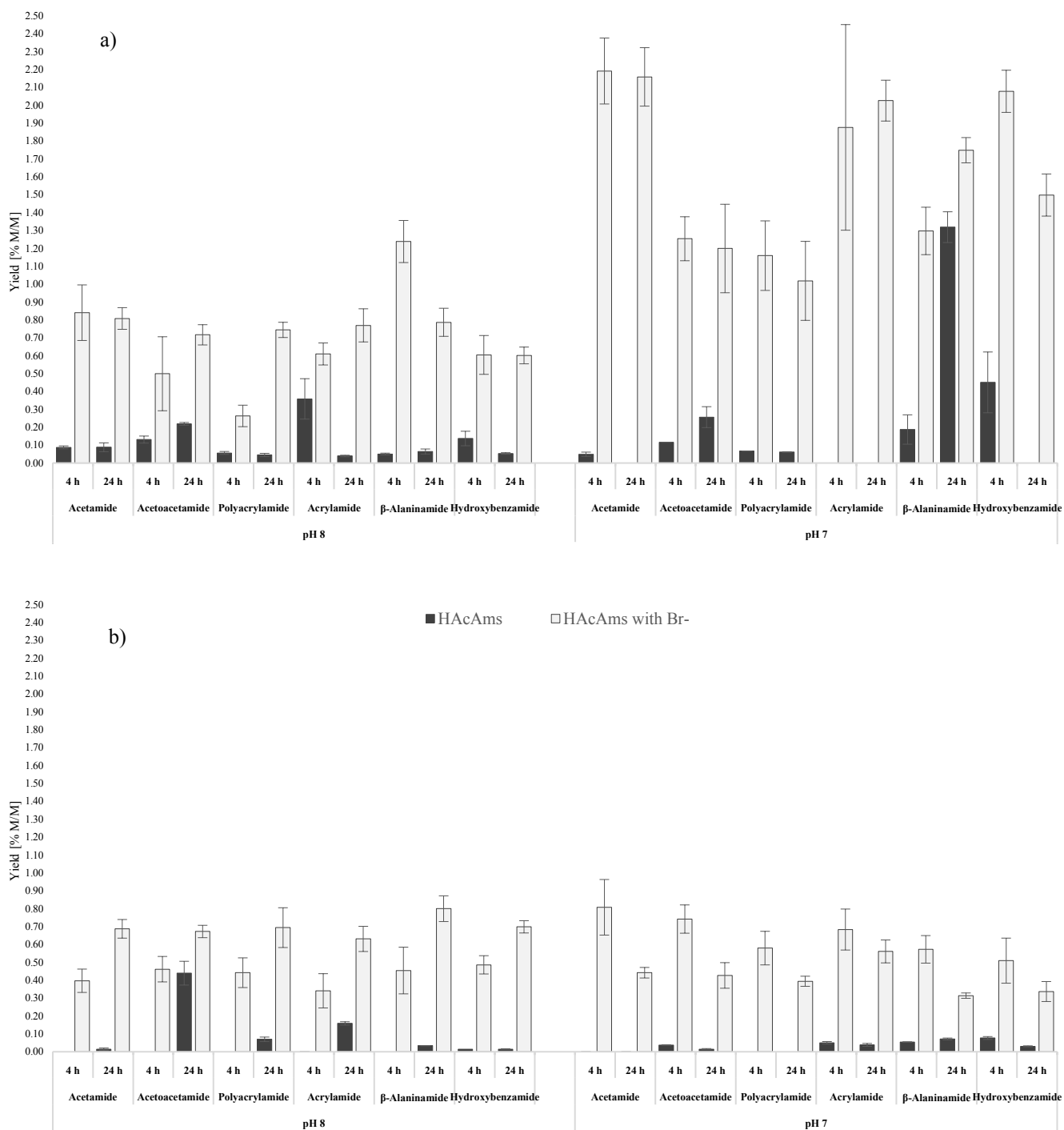


**Figure 5.33:** HAcAms yields from **a)** chlorination and **b)** chloramination under all experimental conditions. Error bars represent the range of duplicate experiments.

### 5.4.2.2 Formation of haloacetonitriles (HANs)

During the detailed phase, and the incorporation of chlorinated and chloraminated samples at pH 7, with retention time of 4 hours and with the addition of bromide, HANs detection was rare. More specifically, during chlorination at pH 7 and during chloramination at pH 8, HAN levels were not detected at all, even after the addition of bromide, as illustrated in **Figure 5.34**. Generally, the majority of HANs were identified at 24 hours, occurred in similar levels between the amide samples, regardless of the profound structural differences and were unaffected by bromide addition during both disinfection methods. Based on the experimental conditions, amides could not have been converted to amines, via reduction or Hofmann degradation (Tanaka and Senju 1976; Clayden et al. 2001), and therefore the presence of HANs cannot be explained via published research and a yet unknown pathway cannot be excluded.

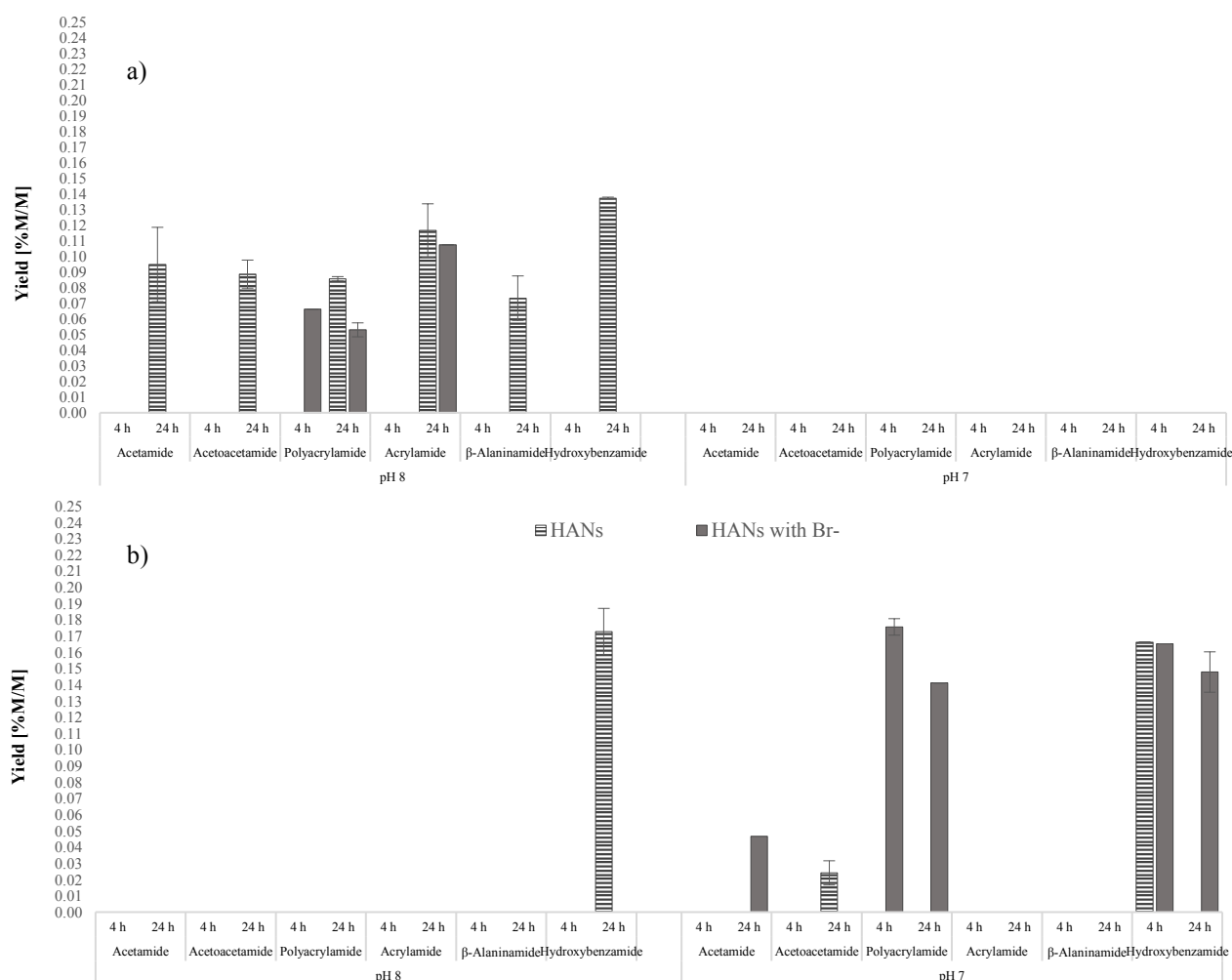


**Figure 5.34:** HANs yields from **a)** chlorination and **b)** chloramination under all experimental conditions. Error bars represent the range of duplicate experiments.

#### 5.4.2.3 Formation of HAAs and THMs

Concerning HAAs, generally it was observed that the presence of bromide ion in the amide samples resulted in higher HAAs yields during both chlorination and chloramination essentially at low retention time of 4 hours. At 24 hours, it was observed that in several cases the yields of HAAs in brominated samples were lower than those with absence of the bromide ion. This was due to the fact that at this retention time HAAs had started to degrade, as previously reported from the occurrence study, while brominated HAAs species are known to be more susceptible to degradation than the chlorinated species (Baribeau et al. 2006). In more detail, with the incorporation of bromide in the analysis, HAAs formation is higher in *acrylamide* (0.79% M/M), closely followed by *acetoacetamide* and *acetamide* all after 4 hours in pH 8. In fact, bromide addition slightly reduced the amount of HAAs formed with time, which resulted mainly from tri-HAAs degradation, whereas pH variation did not influence HAAs fate. The insignificant effect of pH difference has previously been discussed in a study that a range of pH 6-9 had no impact on HAAs decomposition in bromine containing water matrices (Zhang and Minear 2002). Regardless of this trend observed with pH, the findings concerning the fate of HAA yields with retention time were useful to understand further the complex relationship between the HAAs and the corresponding HAcAms. More specifically, HAAs yields tended to increase with time only in samples containing *polyacrylamide* and  *$\beta$ -alaninamide*, while decreased in samples containing *hydroxybenzamide* and *acrylamide* and remained statistically similar in samples of *acetamide* and *acetoacetamide*. If HAAs in amide samples were found only as HAcAms hydrolysis products, then it would be expected to observe reduction in HAcAms yields under the same conditions.

However, even if this happened in the case of  *$\beta$ -alaninamide* samples, it was not observed in the samples of *polyacrylamide*, where total HAcAms increased significantly with time. This finding demonstrated that HAAs may not only form as HAcAms hydrolysis products but amides may also function as independent precursors for HAAs via alternative pathways. Moreover, during chlorination the maximum total HAAs yield (1.05% M/M) was observed in *hydroxybenzamide* samples in pH 7 after 4 hours of retention time. The second most reactive amide compounds were  *$\beta$ -alaninamide* (pH 8, 24 hours) and *polyacrylamide* (pH 7, 24 hours) with yields of 0.78% M/M and 0.70% M/M, respectively.

When amide samples switched to chloramination, significantly lower amounts of total HAAs were generated, in both pH, bromide doses and relative retention times, with reductions ranging 10-92%. This agreed with literature that recommend chloramines as a means to reduce HAAs formation and with other

precursors studies comparing the two disinfection processes. The only amide that did not follow this trend was *hydroxybenzamide*, that either maintained similar yields (pH 8, 4 hours and pH 7, 24 hours), increased (pH 8, 24 hours) or reduced significantly (pH 7, 4 hours) between the two disinfection practices. The most reactive amide became acetamide (0.63% M/M) in pH 8 after 4 hours, and *hydroxybenzamide* (0.53% M/M) in pH 7 after 24 hours. Bromide addition to the chloraminated samples resulted in a minimal decrease in HAAs yields in pH 8 at 24 hours (*by median 20 %*) and relatively low increase in pH 7 (*by median 31 %*) at the same time. This linked to the increased reactivity of chloramines at pH 8 (Kirmeyer et al. 2000), in comparison with that at pH 7 which enhanced the formation/degradation reaction rates in the amide samples. Also, it is interesting, that acetamide samples were slightly encouraging the formation of more HAAs in pH 7 in the presence of chloramines and bromide.

Concerning the yields of THMs in the amide samples, due to an issue with the THM standard mixture, it was not possible to quantify promptly the generation of THMs during chlorination in pH 7, both in samples with or without the addition of bromide. Hence, the impact of bromide ion and disinfection practice were not able to be examined in the case of THMs during chlorination at pH 7. It was expected, though, that in chlorinated amide samples with bromide levels, THMs levels would have been the maximum yielded, as literature and previous thesis findings have demonstrated that chlorination in the presence of bromide levels encourage significantly THMs formation, especially at pH 7 when chlorine is more reactive (Kirmeyer et al. 2000; Liang and Singer 2003; Rodriguez et al. 2004; Hua and Reckhow 2007; Zhang et al. 2010; Bougeard et al. 2010).

So, in chlorinated samples of pH 8 when bromide is present total THMs yields were increasing, except in the case of acetamide where either they were lower or not detected at all. In this case, *hydroxybenzamide* was the most reactive amide generating a total of 0.91% M/M and 0.88% M/M, in 4 and 24 hours, respectively. This observation indicated that the aromatic moiety presented higher reactivity in comparison with the aliphatic amides with regards to THMs formation. This was an important observation, from a practical standpoint, which highlighted that an enhanced removal of aromatic compounds in treated water may efficiently control the formation of the regulated THMs. In addition, the incorporation of bromide resulted into a significant increase of total THMs yields with time in all amide samples, with the most abundant species being dibromochloromethane.

In chloramination, chloroform was detected only in pH 7, with a maximum yield of 0.26 % M/M in samples of  *$\beta$ -alaninamide* after 24 hours of retention time. In general, a significant reduction of total THMs yields

was observed with the alteration of disinfectant method. It was noteworthy that *acetamide* and *hydroxybenzamide* formed chloroform yields below the detection limits. With the addition of bromide in chloraminated samples, total THM yields were identified in both pH and retention times, except in the case of *acetamide* in which no species were detected. Similarly to the chlorinated samples, the most reactive amide was *hydroxybenzamide*, which at pH 7 formed THMs yields of  $0.57\% \pm 0.12$  M/M and  $0.37\% \pm 0.04$  M/M, in 24 and 4 hours, respectively. Hydroxybenzamide presented higher reactivity in comparison with the other selected amides, at pH 8 as well, where a slight increase in THMs yield with time was observed, contrary to pH 7 where yield variances with time were not considered significant, except in the case of hydroxybenzamide.

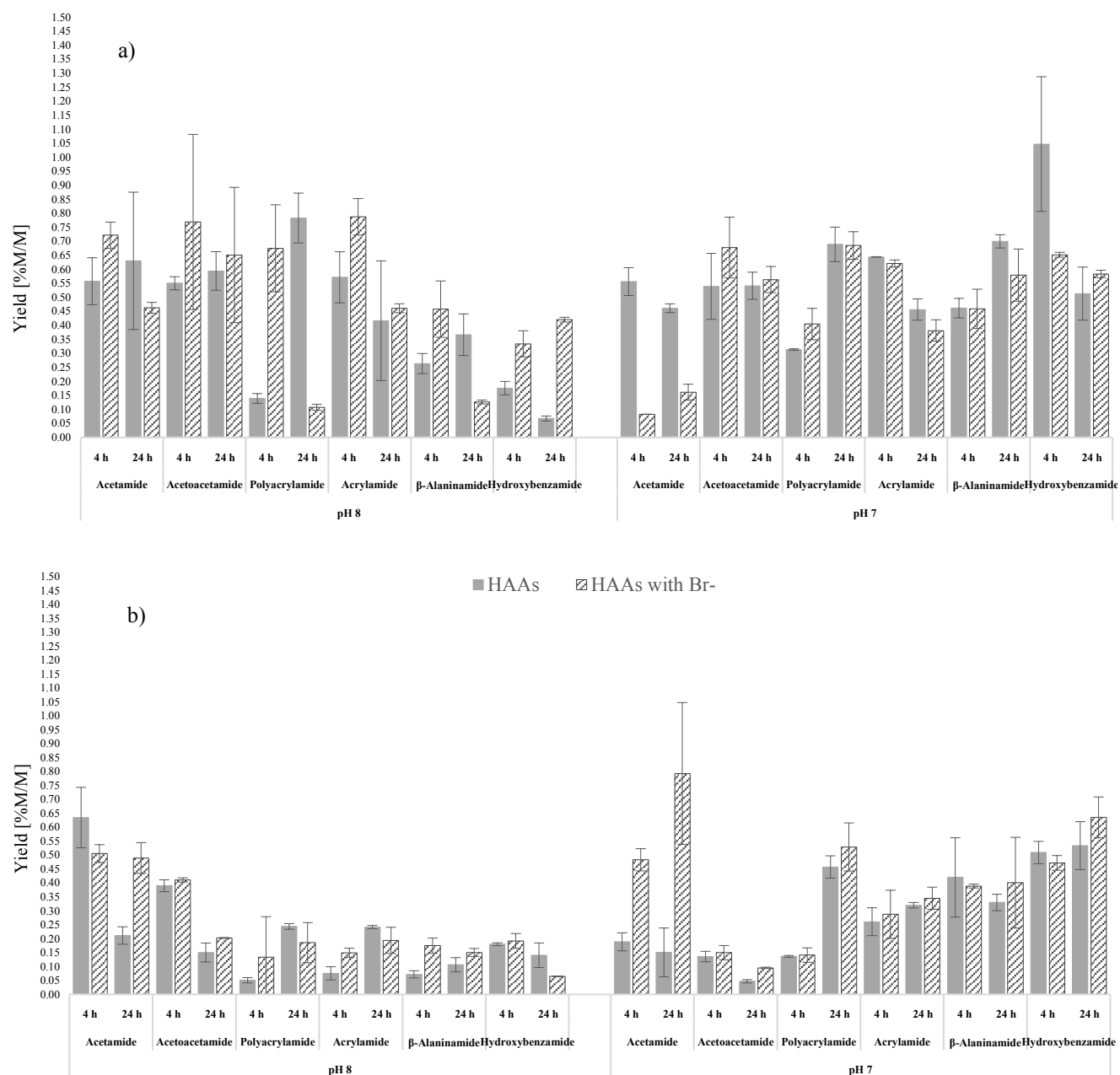


**Figure 5.35:** HAAs yields from **a)** chlorination and **b)** chloramination under all experimental conditions. Error bars represent the range of duplicate experiments.

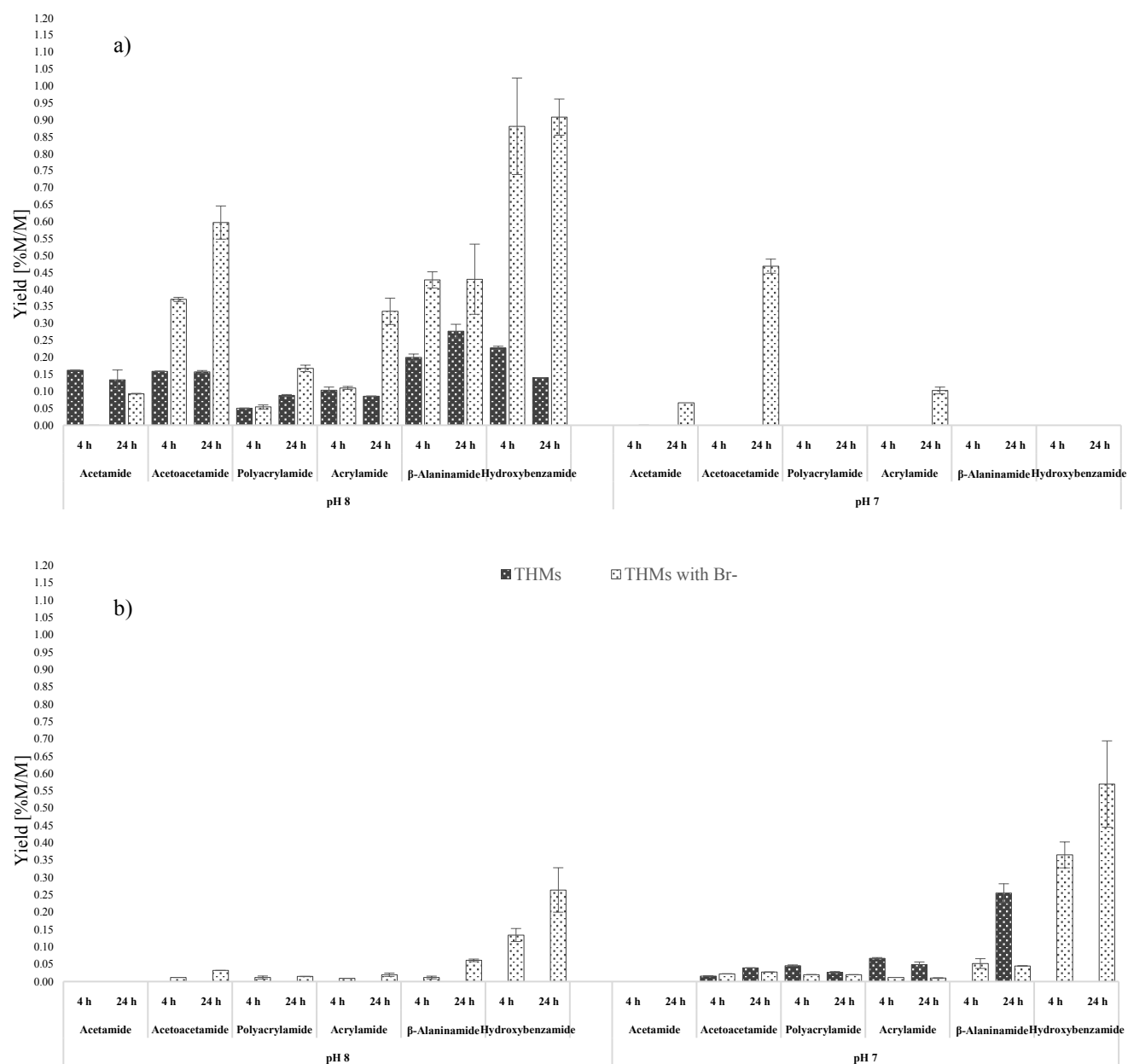


**Figure 5.36:** THMs yields from chlorination and chloramination under all experimental conditions. Error bars represent the range of duplicate experiments.

### 5.4.3 Bromine incorporation in amide samples

The DBPs database from the amide experiments facilitated the examination of bromine incorporation in the DBPs identified. The degree in which bromine is incorporated in the DBPs identified demonstrates the correlation between DBP classes, and is an indication on whether some classes are by-products of others. In addition, understanding the relative formation of different DBP species in the presence of bromide can be useful since brominated DBPs are typically of higher health concern than their corresponding chlorinated analogues (Richardson et al. 2007). The specific DBPs that were identified in this analysis after the addition of bromide dose, were the seven chlorine- and bromine-containing haloacetamides (HAcAms), the seven chlorine- and bromine-containing haloacetic acids (HAAs) and the four regulated THMs. This analysis excluded the bromine incorporation in haloacetonitriles (HANs), and monohalogenated species, as the data was insufficient for further calculations and conclusions. The equations by which the BIF were calculated are found in *Chapter 4.6*. It is known that as the bromide/chlorine ratios increase, the higher is the BIF (Hua and Reckhow 2012), however only one bromide dosed, at 100 µg/L, was added in the amide samples, and therefore the above was not examined in the current study.

The BIF calculations indicated that the amount of bromine incorporation in tri-HAcAms (*median: 0.8*) was significantly higher than that of di-HAAs (*median: 0.4*) during chlorination at both pH 7 and 8. In addition, the BIFs calculated in HAcAms tended to remain similar or increase with retention time at pH 8, with a median of 15%, whereas they tended to decrease at pH 7, with a median 36%. Unlike the dihalogenated species, the incorporation of bromine of tri-HAcAms (*median:0.7*) was lower than that of tri-HAAs (*median: 1.0*), under the same conditions. However, it has to be noted that this trend was observed due to the limited detection of TCAA in amide samples, the only exclusive chlorine containing tri-HAA to balance the equation. The order of median chlorination BIFs of the selected DBPs groups in the amide samples quantified was Tri-HAAs > Di-HAcAms > Tri-HAcAms > THMs ≥ Di-HAAs. This observation was confirmed by Bond et al. (2015) where the highest bromine incorporation was reported in tri-HAAs, however BIF in di-HAAs was calculated higher than that of THMs. In fact, the calculated BIFs in this study were similar (same in several cases) between THMs and di-HAAs, however the rank included THMs first due to their slight increased BIF at pH 7 (**Fig. 5.37**).

In chloraminated samples, similarly to the chlorinated ones, BIF values indicated that bromine incorporation into tri-HAcAms (*median:0.8*) was significantly higher than that of di-HAAs (*median: 0.5*), except in the acetoacetamide samples, where the opposite was observed. This suggested the presence of an alternative pathway to the formation of HAAs from the model amides rather than HAcAms hydrolysis, only. Furthermore, the BIFs calculated in di-HAcAms presented the tendency to increase with residence time in pH 8 (*by median 20.4%*), and decrease at pH 7 (*by median 45.6%*). Since the same pattern (and similar percentages) with residence time was observed in chlorinated and chloraminated systems, this indicated that the effect of disinfectant was of secondary importance, and that reactions were more dependent on pH. Nonetheless, HAcAms are reported to be less stable at pH 8 and therefore the increase of BIFs indicated that chlorinated species occurred at lower levels (UK WIR 2014). Concerning the BIFs of tri-HAcAms in chlorination (*median: 0.9*) was lower than that of tri-HAAs (*median: 0.7*), under the same conditions. Median BIFs for THMs decreased between chlorinated and chloraminated amide samples, from 0.4 to 0.1, respectively (**Figure 5.37**). The order of median chloramination BIFs of the selected groups was very similar to that of chlorination, Tri-HAAs > Di-HAcAms > Tri-HAcAms > Di-HAAs > THMs. To the author's knowledge, this is the first time that HAcAms (*7 species*), HAAs and THMs BIFs values are compared and ranked during both chlorination and chloramination of organic compounds.

Overall, with the exception of THMs, BIF values in chloraminated samples, for HAAs and HAcAms, were generally slightly higher than in chlorinated samples. This trend was most prominent for di-HAAs, from the previously reported highly reactive *acetoacetamide* and *hydroxybenzamide*, where median BIFs were respectively 65% and 26 % higher in chloraminated than in chlorinated samples. Therefore, even though chloramination virtually reduces DBP yields, at the same time enhances bromide incorporation in classes such as HAAs and HAcAms, and switches speciation towards more brominated species suspected of higher health significance. In addition, from the order of their chlorinated and chloraminated BIFs, it was highlighted that bromine incorporation is more prominent in DBP classes currently non-regulated in the European Union, such as HAAs and HAcAms.

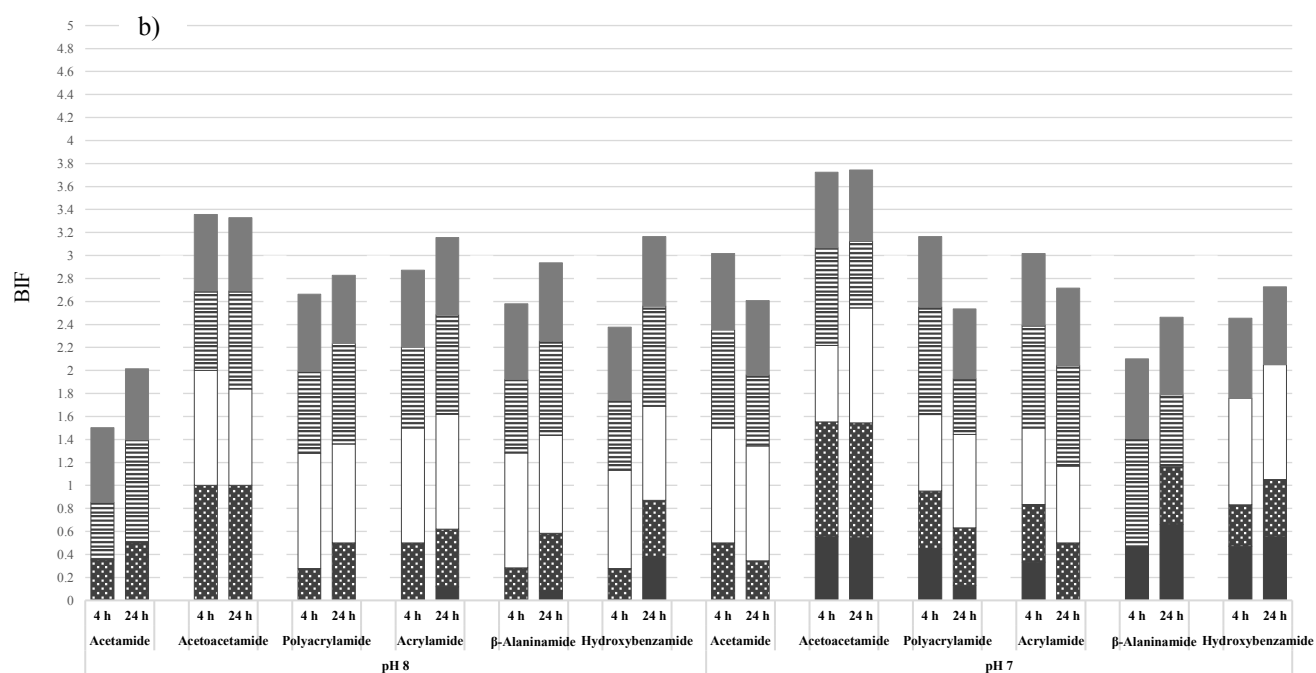
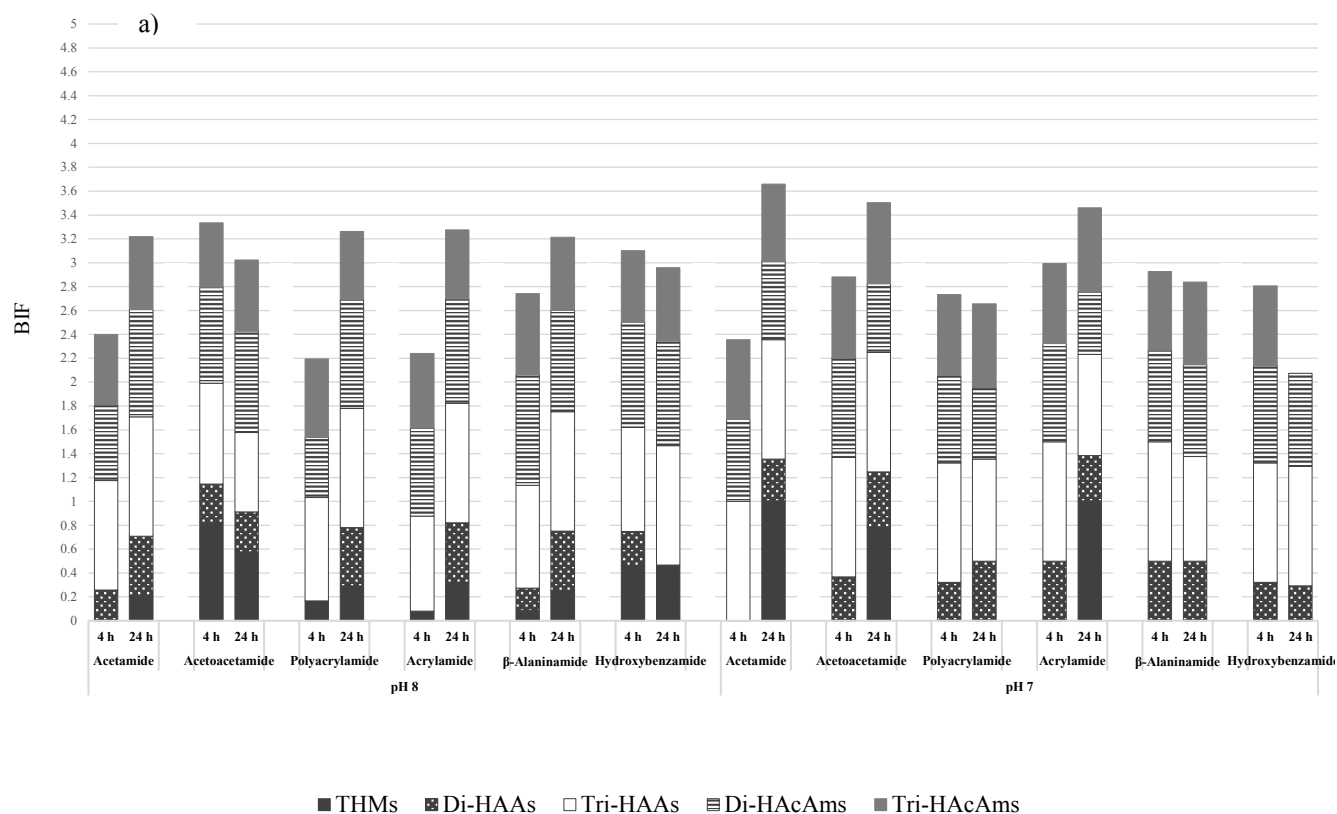


**Figure 5.37:** Bromine Incorporation Factor (BIF) in **a)** chlorination and **b)** chloramination of amides.

## Chapter 6. Discussion

This PhD research aimed to achieve an improved understanding of regulated and unregulated DBPs in terms of their occurrence and fate in drinking water distribution system. To-date research has focused in investigating the behaviour of the regulated THMs and HAAs in distribution networks, however there was sparse and inconsistent information on the fate of the non-regulated HANs and HAcAms in chlorinated and chloraminated systems.

### 6.1 Trends of regulated and unregulated DBPs in drinking water distribution

The database generated during the annual monitoring program in four water treatment works in England and their downstream locations, suggested that the regulated THMs levels ranged from 20.5-71.0 µg/L between 6 and 106 hours (median: 43 µg/L) in chlorinated systems, whereas in chloraminated systems ranged from 14.6-37.1 µg/L between 6 and 106 hours (median: 27 µg/L). Regardless of the disinfection practice, total THMs concentrations were always increased with increasing water age, whilst chlorine residual was decreased (Baribeau et al. 2006). This trend was observed during all seasonal sampling rounds at all four chlorinated and chloraminated systems, and this was consistent with previous published work and the company's historical data. The results from the actual distribution networks sampling indicated that THM concentrations were significantly high, exceeding the water utilities internal limit of 50 µg/L, particularly in the downstream locations characterised by high water ages and during the months with higher temperatures. Brominated species (e.g. dibromochloromethane, bromoform) represented most of the THM concentrations in these systems, because of the bromide concentrations present in the final water of these systems, with the most abundant trihalomethane being dibromochloromethane. Concerning the occurrence of HAAs, currently not regulated in the EU, levels ranged respectively, between 9.8-66.9 µg/L (*median: 33.5 µg/L*) and 9.5-53.7 µg/L (*median: 30 µg/L*) from 6 to 102 hours, in chlorinated and chloraminated systems. A general observation is that concentrations were not characterised by significant changes within the distribution system, as in some cases the initial HAAs formed at 6 hours were similar to those observed after 72-106 hours, albeit with intermediate fluctuations. Both THMs and HAAs were seasonally dependent, with significant higher yield during the sampling round with the highest temperature (22°C) and the lowest yield during the lowest water temperature (8°C).

Moreover, concerning the occurrence and behaviour of the non-regulated HANs and HAcAms, comparable levels were quantified during all sampling rounds in all downstream locations sampled. When these concentrations were compared against those of THMs and HAAs, N-DBPs occurred in significant lower amounts, and represented almost 10% of the THMs and 11.5% the HAAs (Krasner et al. 2006). In chlorinated systems, HANs were found at the median sum concentrations with 4.8 µg/L, followed by HAcAms with 4.0 µg/L, whereas in chloraminated systems HANs occurred in significant lower yields with median 1.5 µg/L and HAcAms with 3.8 µg/L. The N-DBP concentrations identified in this study largely agreed with the ranges detected from a previous nationwide occurrence survey in England (Templeton et al. 2012; Bond et al. 2015), in which HANs and HAcAms (3 species) reported with mean concentrations of 3.2 µg/L and 1.5 µg/L, respectively. In addition, the N-DBP results were comparable with those identified in a previous US DBP survey by Krasner et al. (2006), where HANs (5 species) and HAcAms (5 species) were reported in levels of 3 µg/L and 1.5 µg/L, respectively. It was noteworthy that both HANs and HAcAms levels were unaffected by seasonality and water temperature, which indicated that other parameters like precursor characteristics functioned as a more important factor in the formation of these DBPs. As previously discussed in other studies, increased water temperature is associated with increased reaction rates, disinfectant consumption and demand, which leads to increased levels of THMs and HAAs (Singer et al. 2002; Rodriguez et al. 2004; Baribeau et al. 2006; Bond et al. 2012). However, since this was not observed for HANs and HAcAms, on a fundamental basis, this indicated that the formation of these DBP classes is also independent from disinfectant dosage.

Overall, it was observed that the total HAN and HAcAms concentrations reported in the early stages of distribution were similar or slightly higher than at the final stages, regardless of the intermediate minimal fluctuations. From the correlation factors and the levels, themselves, it was concluded that the intermediate decreases of HANs were not necessarily linked with HAcAms, and therefore HAcAms were generating also from independent precursors.

## 6.2 Advantages & Disadvantages of SDS tests in predicting DBPs in distribution

Together with the actual monitoring of the selected water works and downstream locations, simulated distribution system tests were simultaneously implemented with the use of the same water matrices. However, the SDS tests assume zero contribution from the distribution system parameters since this was practically a bottle incubation process, and therefore cannot account for possible interaction between the bulk water and the network environment (US EPA 1997). The aim was to validate SDS tests for HANs and HAcAms in both chlorinated and chloraminated systems, by mimicking the exact operational conditions and subsequently collect abundant information on the simultaneous prediction of THMs, HANs and N-DBPs. In addition, the implementation of SDS was considered as a useful tool for water utilities to investigate the impact of potential changes in operational practices, such as switching from chlorination to chloramination, on the expected DBP formation. Besides, water utilities lack monitoring and action tools at their disposal to predict DBPs in distribution, and proactively adapt and operate their plants, to control DBP formation.

Overall, when the results of the SDS tests were compared against those from actual distribution systems, it was observed that the tests predicted the formation and variations of THMs, HAAs, HANs and HAcAms in both chlorinated and chloraminated systems during all sampling rounds. In addition, another main finding was that the tests simulated well the speciation, and bromine incorporation in the selected DBPs in the distribution networks. In more detail, SDS tests accurately predicted THMs fate but slightly underestimated their concentrations, mainly during chlorination (*median deviation: 8.6%*) and to a lesser extent during chloramination (*median deviation: 8.6%*), which from a practical standpoint was minimal. The implementation of SDS tests by Koch et al. (1991) were not conclusive on the expected deviation, whereas Brereton 1998 observed relative overestimation. Furthermore, the SDS results on HAAs showed that the tests simulated well the formation/ decay patterns of HAAs in simulated distribution systems, as in US studies (Obolensky and Frey 2002) and suggested that the implementation of this tool by water utilities will give a good estimation of the occurrence levels to be expected at the final location the system within 6 hours, whereas the maximum concentrations could be identified between 24 and 48 hours. Similarly, but in more instances to THMs, SDS tended to underestimate the levels of HAAs in chlorinated and chloraminated distribution systems, which is in line with the findings from a UK study by Graham et al. (2009). These deviations were likely due to the tests limitations but also due to the wide ranges of water age modelling in which actual samples were taken. The accurate prediction of the above DBP classes,

already known to be predicted by SDS tests, validated this tool and enabled its assessment with regards to HANs and HAcAms in chlorinated and chloraminated systems for the first time. Interestingly, the predicted levels of HANs and HAcAms reported from the SDS were statistically similar with those quantified in the actual distribution samples during all sampling rounds. Nonetheless, some deviations were observed, especially in low water ages, where SDS slightly overestimated HANs levels in distribution in both chlorinated and chloraminated systems, however was minimal from a practical viewpoint, with the largest difference being 2.1 µg/L. Concerning the key question on the prediction potential of SDS for HAcAms, the tests predicted to a high extent the formation, decomposition and speciation of these N-DBPs. Namely, in the two simulated chlorinated systems the total median yields were 3.6 µg/L (3.4 µg/L in actual distribution samples) and 3.5 µg/L (4.0 µg/L in actual distribution samples). Likewise, in the two chloraminated systems the total median yields were 4.0 µg/L (3.9 µg/L in actual distribution samples) and 3.6 µg/L (3.7 µg/L in actual distribution samples). The deviations between the actual and simulated samples were statistically minimal and ranged between 0.1-2.6 µg/L, averaging 1.2 µg/L, therefore SDS tests predicted, even conservatively, the total HAcAm levels to be expected in the selected water ages (6-106 hours).

The implementation of SDS tests in chloraminated systems presented higher level of accuracy in comparison with those chlorinated. However, this was not necessarily linked with the disinfection practice itself but rather to the samples handling in disinfection. As previously mentioned in *Chapter 5.2.2*, the SDS samples for the chloraminated systems were sampled and incubated directly after the disinfection stage *in situ*, to represent the application of in-line chloramination by the water utility, which could not have been performed in the lab. On the other hand, the SDS samples for the chlorinated systems were collected prior to disinfection and were chlorinated in the lab with sodium hypochlorite solution. This difference in SDS sample handling between the two disinfection practices may explain why DBPs prediction in chloraminated samples was more precise. Nevertheless, the target DBPs also presented different levels of occurrence accuracy in the SDS tests of this study, and their order was THMs > HAcAms > HANs > HAAs.

Prior to the validation of SDS tests for the two N-DBP classes selected in this study, there were important knowledge gaps on the combining and individual impact of water temperature, disinfectant contact time and concentration, and water age, for which now there is an improved understanding.

### 6.3 Advantages & Disadvantages of chloramines for minimising DBPs in distribution

The validation of the SDS tests not only helped in creating the most updated database on the expected occurrence and behaviour of 25 DBP species in distribution, but also facilitated further experiments that contribute to new knowledge with regards to the impact of potential disinfection alteration on DBPs formation. Even though switching from chlorine to chloramines has been a widely proposed strategy to effectively control the formation of the regulated THMs and HAAs in drinking water, there is conflicting literature on whether in fact chloramines encourage the formation of the more cytotoxic and genotoxic HANs and HAcAms (Bond et al. 2011; Krasner et al. 2012; Huang et al. 2017). To-date, the performance of the two disinfection methods has been mainly compared either from real water treatment samples that usually have different source waters or from artificial water matrices, and thus present a level of inconsistency. The novelty of this work package was based on the direct comparison of DBP levels to be expected in the same distribution systems, between the current disinfection practice and the potential alternative practice, via the implementation of SDS tests. In addition, it provided a useful insight on operational strategies for current and future regulatory compliance.

Overall, switching from chlorine to chloramines in the currently chlorinated systems, formed lower THMs, HAAs, HANs and HAcAms levels during all the sampling rounds that it was performed. Even though this pattern was expected for THMs and HAAs (Cowman and Singer 1996; Diehl et al. 2000; Karanfil et al. 2007; Bougeard et al. 2010; US EPA 2010; UK WIR 2014), the results indicated that chloramination did not enhance the occurrence of HAcAms and especially of HANs, as suspected by water professionals. Therefore, this was a confirmation that the nitrogen atom in N-DBPs may come primarily from the organic nitrogen content present in water matrices, rather than from the ammonia added during chloramination. In numbers, switching from chlorine to chloramines, reported median decreases of 33%, 48%, 60% and 50%, in THMs, HAAs, HANs and HAcAms, respectively. However, it was observed that chloramination minimised DBP levels at the same time increased the bromide incorporation in HAAs and HAcAms, which is an important observation with conflicting interests between water industry and epidemiologists. From a practical standpoint, this means that if HAAs are regulated, water utilities that use or are planning to use chloramines should investigate this issue further to avoid concentration exceedances. The enhanced bromine incorporation observed mainly for HAAs and HAcAms in chloraminated systems is possibly linked to multiple factors. The first is that the chloraminated systems had typically higher bromide levels: the median concentration being 55 µg/L, versus 15.5 µg/L in chlorinated systems (**Table 5.1**).

Secondly, small amounts of free chlorine present during chloramination, may have led to higher bromine/chlorine ratio, in comparison with the same ratio during chlorination (Hua and Reckhow, 2012). In any case, the simultaneous presence of chloramines, bromamines, free chlorine and free bromine during chloramination in the presence of bromide levels makes identifying the active oxidation and halogenation agents a difficult issue (Diehl et al., 2000; Duirk and Valentine, 2007).

Moreover, as a validation, and further assessment of the current disinfection practice in the selected systems, the two commonly chloraminated systems were chlorinated. The results from switching from chloramines to chlorine, reported median increases of 28% in THM, in 30% in HAAs, 50% in HANs and 42% in HAcAms, which demonstrates the wise choice of the water utility to apply chloramines in these systems as a means to control DBPs formation. Nevertheless, water utilities considering switching to chloramines should ensure optimum chlorine to ammonia ratio in their systems, to prevent taste and odour issues, lead release (though there would be low risk if orthophosphate is applied in WTW), and possibly nitrification within the distribution system (higher risk in warm climates) (AWWA 2013).

## **6.4 The importance of understanding DBPs precursors**

Once the occurrence, fate and key formation factors of DBPs in distribution were analysed, it was observed that the relative importance of the composition of the organic matter, widespread in water networks, could not be evaluated. In addition, the absence of DBP data during the direct chlorination and chloramination of amides (Bond et al. 2012), provided an interesting knowledge gap in the field of independent HAcAms precursors. Thus, the relative effect of six model amide precursor compounds to act as organic precursors principally for N-DBPs and for HAAs and THMs, upon chlorination and chloramination, under a range of water quality conditions (pH, bromide dose and water age) was investigated in controlled lab conditions. From the results of this experiment, HAcAms and HANs yields, as well as HAAs and chloroform yields were observed from all selected amides during both chlorination and chloramination. The results indicated that HAcAms form independently from HANs hydrolysis, and amides present in humic substances or chemicals added to water may function as independent HAcAm precursors. This finding is in line with similar model compound studies by Huang et al. (2012) and Chu et al. (2016). Besides, HANs yields, BIFs and fluctuations presented poor correlations with those of HAcAms, and were not expected to be generated. The fact that chloramination does not necessarily induce the formation of more HAcAms was also confirmed by the precursor study. In addition, when amide samples were chloraminated, significant lower

amounts of total HAAs were generated, with both pH, bromide doses and relative retention times, with reductions ranging 10-92%, similarly to THMs. As expected from the actual distribution sampling and the SDS tests, THMs increased with retention time, between 4 and 24 hours in all model amide experiments. In general, from the SDS tests it could be said that HAAs presented an increase in their yields until 24 hours during both chlorination and chloramination, however this was not also observed in all the amide tests, where several amide samples presented HAAs decomposition with time. Likewise, HAcAms yields in chlorinated systems generally increased until 24 hours, whereas in chloraminated systems the yields decreased. Once more, this was not the general observation in the amide precursor experiments. The fact that amide tests did not represent the behaviour of HAAs and HAcAms formation/decay pattern as in distribution system was expected due to the fact that actual water samples consist of various other elements that may counterbalance the individual impact of amide compounds present at a given water age.

The findings also highlighted the importance of the precursor's structure in relation with the chemical functionality, since the highest HAcAms yields were reported during chlorination, with the addition of bromide in aliphatic amides. The aromatic nature of hydroxybenzamide was found to be a more important precursor for THMs rather than HAcAms and HAAs, for which aliphatic amides containing carbonyls were more significant. In fact, during chloramination, the increasing number of carbon atoms of the aliphatic amides facilitated the formation of HAcAms, however the aromatic amide (*hydroxybenzamide*) presented low molar yields. This suggested that if water utilities are interested in controlling the formation of the regulated THMs, should focus primarily on removing the aromatic precursors in raw water. The opposite strategy, mainly removing aliphatic moieties, would be the suggested practice if water utilities were interested in controlling HAAs and HAcAms levels. An important indicator to assess the reactive portion of TOC in water matrices is SUVA, where values  $> 2$  indicate high aromatic nature. If we have a look at the calculated SUVA of our annual monitoring survey (Appendix A.7), there were several cases in which this was observed, especially in WTW C and D (both chloraminated), which were initially selected due to their high risk in generating THMs. Therefore, the findings of the model compound tests and the actual sampling data feed one another and provide an improved understanding of a least identified parameter to explain high and possibly unexpected THM levels in treatment works;  $SUVA > 2$  means aromatic structures in the NOM  $\rightarrow$  aromatic precursors increase THM levels  $\rightarrow$  WTW that present  $SUVA > 2$  have increased THM levels even during chloramination.

Furthermore, the results indicated that the predominant mechanism to form N-DBPs was the incorporation of halogens in the nitrogen-containing amides and not the incorporation of inorganic nitrogen from the chloramines, something that was initially suspected from the actual distribution monitoring and SDS tests analysis. This observation is also discussed in studies that compare haloacetamides yields of nitrogen and non-nitrogen containing precursors (Nihemaiti et al. 2016; Le Roux et al. 2016). From the calculated BIFs in HAcAms and HAAs, it was found that amide samples exhibited slightly increased bromine incorporation during chloramination in comparison with chlorination. Therefore, if these DBPs are regulated, water utilities should investigate further their potential to form elevated brominated species in their systems with the use of chloramines. The order of median chlorination and chloramination BIFs of the selected DBPs groups in the amide samples quantified was Tri-HAAs > Di-HAcAms > Tri-HAcAms > THMs ≥ Di-HAAs.

## 6.5 Implications for the water industry and recommendations for future research

An interesting point was that the five HAAs species currently regulated in the US, did not always represent a significant proportion of the total HAAs (*9 species*), especially in WTW with medium to high bromide levels, which highlighted the importance of the inclusion of all nine species in DBP monitoring surveys for accurate observations. In more detail, in water plants characterised by low to medium bromide levels the proportion of the total HAAs comprised of the HAA<sub>5</sub> ranged between 54.9-83.1% (*median 67.3%*) and 52.8-76.9% (*median 67.9 %*). On the other hand, in water treatment plants characterised by medium to high bromide levels (in the context of the UK water industry), the same proportion was 36.8-85.0% (*median 64.9%*) and 52.7-78.9% (*median 59.7 %*). The above has been previously discussed by a previous study (Baribeau et al. 2006), that included water works with relatively low to medium levels (10-30 µg/L), and reported similar percentile representation of HAA<sub>5</sub> of 26-80%. In addition, the fact that this conclusion has been highlighted in other studies (Singer et al. 2002; Singer 2006), suggests that future regulatory activity for incorporation of HAAs in the EU directive (or review of the current regulations in the US), will possibly be directed towards all nine HAAs species. If total HAAs are incorporated in the internal monitoring protocol of water utilities, a marker value of 60 µg/L should be considered, as already advised by US EPA (2010). In any case, the N-DBP database generated suggested that HANs and HAcAms in UK drinking water form at similar levels as in other regions and were safely below the guideline values by WHO (2011) for DBAN (<70 µg/L) and DCAN (<20 µg/L).

Also, the validation of SDS tests to predict in varying degrees the fate of THMs, HAAs, HANs and HAcAms has facilitated the assessment of various other potential operational alterations. For instance,

research in the field can combine SDS tests to investigate the impact of advanced oxidation processes (AOPs), UV disinfection, or even boosting disinfection, in the formation of DBPs.

Furthermore, the presence of bromide was reported to increase the sum concentration of both regulated and unregulated DBPs, by even two-fold, and has been highlighted as one of the most important formation factors (Amy et al. 1991; Symons et al. 1993; Cowman and Singer 1996; Baribeau et al. 2006). In addition, the potential of chloramines to inhibit the formation of more brominated HAAs and HAcAms species, even at low bromide levels, raises concerns for water utilities and epidemiologists, especially if HAAs are included in the regulation. Therefore, future research should focus in optimising current technologies, such as activated carbon, ion exchange resins, aluminium coagulation, electrochemical oxidation (graphite) (Watson et al. 2012; Sun et al. 2013) or investigate innovative and cost-effective technologies to remove bromide ions from treated water prior to disinfection.

To-date, the limited and inconsistent DBP concentration data in distribution has made it impossible to conduct epidemiological research to attempt to relate the importance of exposure to these DBPs to human health. The large database, that has been created for the purposes of this research and presents the advantage of including DBP levels both real and simulated distribution system, can also be combined with health outcome databases (e.g. cancer, infant birth weight) for the same regions, to begin to assess the health significance of the range of DBPs at the levels at which they occur in tap waters.

On a different topic, from the seven selected HANs, only five of them were identified, therefore total concentrations of the nine species are anticipated to be higher in reality, whereas from the nine HAcAms, eight were identified with the analytical methods applied. Indeed, the improvements in analytical laboratory procedures have recently enabled the quantification of these compounds, however important limitations towards efficient DBP monitoring is the time consuming and expensive laboratory procedures, therefore future research can optimise chromatography to simultaneously identify a wide range of DBPs both rapidly and precisely (Alexandrou et al. 2017) or design accurate online monitoring tools. Also, research in the field can extend current mathematical prediction models to include the recently identified DBPs and incorporate more variables (water age, bromide levels, disinfectant type) (Sadiq and Rodriguez 2004; Bridgeman et al. 2010; Chowdhury et al. 2011; Zhang et al. 2011) although these models tend to be quite water-specific, they can be useful for water utilities to better understand the DBP formation in their systems.

## Chapter 7. Conclusions

The conclusions of this study, representing important new contributions to knowledge, are:

- ◆ Simulated distribution system tests accurately and simultaneously predict the occurrence and speciation of THMs, HAAs, HANs and HAcAms to be expected in both chlorinated and chloraminated systems. While this was already known for THMs and HAAs, this is the first time these tests were shown to be able to successfully predict the levels and speciation of HANs and HAcAms.

Therefore, SDS tests are recommended to water utilities not only to estimate the levels of these regulated and unregulated DBPs in distribution systems, but also proactively design and adjust operational distribution practices, such as switching the residual disinfectant type.

- ◆ Whereas THM concentrations significantly increase with water age in both chlorinated and chloraminated systems, generally, HAA, HAN, and HAcAm concentrations increase much less with water age, with levels identified in the early stages of distribution (6 hours) either similar or slightly higher at the final stages (72 and 106 hours), regardless of the intermediate occurrence fluctuations. The exception to the above rule is the class of HAAs that decrease between 6 and 106 hours upon chloramination.

These overall distribution increases differ between the two disinfection practices. Upon chlorination THMs, HAAs, HANs and HAcAms increased by mass median 62%, 14%, 35% and 30%, respectively. Upon chloramination THMs, HANs and HAcAms increased by median 50%, 33% and 20%, respectively, while HAAs decreased by median 5%. The main take home message was that water age is one of the most important factors that determines the occurrence of both regulated and unregulated DBPs in distribution systems in varying degrees. Therefore, a comprehensive framework to control the formation of DBPs in water networks should also include strategies of minimising water age when possible.

- ◆ THMs and HAAs present high seasonal dependence whereas HANs and HAcAms present relatively similar levels between sampling rounds and at different water temperatures. This highlights that, on a fundamental basis, the formation of HANs and HAcAms in distribution systems was influenced by other factors; primarily by the amount and nature of water matrix constituents and disinfection practice,

to a lesser extent on disinfectant contact time, and was relatively unaffected by water temperature and disinfectant dose.

- ◆ The presence of bromide significantly increases the formation of all the studied regulated and unregulated DBPs and shifts the speciation to more brominated species. This finding is important from a health standpoint, since brominated DBPs are suspected of being more cytotoxic and genotoxic.

It is noteworthy that even though chloramination is suggested as a minimisation strategy, it was reported to lead to greater bromine incorporation than chlorination for HAAs, HANs and HAcAms. This finding indicates that bromine is incorporated into these classes more effectively than chlorine, thus increasing the health concerns associated with DBPs.

- ◆ The implementation of chloramines as a final disinfectant results in significant decreases in THM, HAA, HAN and HAcAm levels. Switching from chlorine to chloramines resulted in median decreases of 33% in THMs, 48% in HAAs, 61% in HANs and 51% in HAcAms by mass. This suggests that the nitrogen in N-DBPs originates primarily from the nitrogen that is naturally present in source water rather than the nitrogen in the introduced ammonia during chloramination.
- ◆ HAcAms have different precursors from HANs and HAAs, and form independently from the hydrolysis of HANs, via alternative pathways during chlorination and chloramination, namely direct chlorination of amide groups and incorporation of inorganic nitrogen in amide structures. In addition, even though HAAs are generated to some extent as HAcAm hydrolysis products, their formation patterns also suggested alternative pathways.
- ◆ The direct chlorination and chloramination of six amide precursors generate HAcAms, HANs, HAAs and THMs yields in varying degrees, via enolization and/or N-chlorination.  
Relative to chlorination, the median aggregate formation (i.e. the sum of all individual precursor yields) of THMs, HAAs, HANs and HAcAms were reduced by respectively 66.5% and 50.9% across the two pH levels (8 and 7) without the presence of bromide, and by 46.4% and 45.5% with the presence of bromide, by instead applying pre-formed chloramines. The formation of total HAcAms dramatically decreased with increasing pH during both chlorination and chloramination, however the formation of the other DBP classes was relatively insensitive to pH alteration.

As expected, the addition of bromide in amide samples resulted in significant increases in the median aggregate formation of the selected DBPs in pH 7 by 70% and 64 % during chlorination and chloramination, respectively, whereas in pH 8 these increases were 50% and 72%. The most reactive amide precursor in chlorinated samples was hydroxybenzamide (aromatic amide) followed by acetoacetamide (pH 8) and acrylamide (pH 7), whereas in chloraminated samples the most reactive amides were hydroxybenzamide and acetamide at both pH values.

The findings of this study confirmed that the N-oxidation of amide structures is a potential mechanism for HAcAms formation, which may also occur completely separately from HAN hydrolysis. This suggests that if precursor removal is to be used as a treatment strategy for minimising HAcAms and HANs, the success in minimising these groups of N-DBPs may differ based on the relative success in removing their independent precursors.

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## Appendices

### Appendix A. Supplementary Information about the Materials and Methods

**Table A. 1:** Preparation of sample & analysis containers.

| <b>Preparation of glass sample bottles and vials</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"><li>• Rinse the container with 100 mL of chromic acid solution- <math>\text{H}_2\text{CrO}_4</math>, returning the chromic acid to its original container after use. Then rinse with at least three 100-mL portions of tap water.</li><li>• Machine wash in accordance with the machine manufacturer's instructions using a detergent and 90°C water.</li><li>• Remove the bottles from the machine and rinse them with two 100-mL portions of HCl (1+2), followed with three 100-mL portions of water.</li><li>• Heat for a minimum of 4 h (mouth up) in a forced draft oven at 275 to 325°C. Upon cooling, fit the bottles with caps and the vials with septa (ASTM, 2011).</li></ul>                     |
| <b>Preparation of extraction glass vials, caps &amp; septa</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
| <i>Extraction glassware must be thoroughly cleaned</i> (Hautman 1997; Munch and Hautman 1995)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |
| <ul style="list-style-type: none"><li>• Clean all glassware as soon as possible after use by rinsing with the last solvent used in it.</li><li>• Follow by washing with hot water and detergent and thoroughly rinsing with tap and reagent water.</li><li>• Drain and dry in a laboratory dryer at 4°C for a day or muffle furnace at 60°C for one hour.</li><li>• Insert the glassware in a solution HPLC grade Nitric acid.</li><li>• Rinse three times with tap water and then with RO water.</li><li>• Drain, dry or heat in a lab dryer at 4°C for a day or muffle furnace at 60°C for one hour.</li><li>• After drying and cooling, seal and store all glassware in a clean environment free of all potential contamination.</li></ul> |

**Table A. 2:** Solution preparation and procedure for N, N-diethyl-p-phenylene diamine [DPD] – ferrous ammonium sulphate [FAS] Method.

For the implementation of this method several solutions should be prepared upfront;

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                                                                                                      |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p><b>Solution A: Phosphate buffer solution</b></p> <ul style="list-style-type: none"> <li>• Dissolve 24 g <math>\text{Na}_2\text{HPO}_4</math> and 46 g <math>\text{KH}_2\text{PO}_4</math> in distilled water.</li> <li>• Dissolve 800 mg disodium EDTA in 100 mL distilled water.</li> <li>• Mix these two solutions.</li> <li>• Dilute the mixing to 1 L of distilled water.</li> <li>• Add 20 mg <math>\text{HgCl}_2</math> (<i>preservative</i>).</li> </ul> | <p><b>Solution B: DPD indicator solution</b></p> <ul style="list-style-type: none"> <li>• Dissolve 1.5 g p-amino-N, N-diethylaniline sulphate in distilled water.</li> <li>• This distilled water contains 8 mL of 1+3 <math>\text{H}_2\text{SO}_4</math> (<i>Solution D</i>) and 200 mg disodium EDTA.</li> <li>• Dilute to 1 L.</li> <li>• Store in a coloured, glass-stoppered bottle.</li> </ul> |
| <p><b>Solution C: Ferrous ammonium sulphate (FAS) titrant</b></p> <ul style="list-style-type: none"> <li>• Dissolve 1.106g Mohr's salt (ammonium iron sulphate, <math>\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2</math>) in distilled water.</li> <li>• This distilled water contains 1 mL of 1 + 3 <math>\text{H}_2\text{SO}_4</math> (<i>Solution D</i>).</li> <li>• Dilute to 1 L.</li> </ul>                                                                      | <p><b>Solution D: Sulphuric acid solution [1 + 3]</b></p> <ul style="list-style-type: none"> <li>• Slowly add one part of <math>\text{H}_2\text{SO}_4</math> (sp. gr. 1.84) to three parts of distilled water.</li> </ul>                                                                                                                                                                            |

The DPD-FAS titrimetric method steps are the following;

- Place 5 mL of phosphate buffer (A) in a titration flask.
- Add 5 mL of DPD indicator (B).
- Add approximately 1 g of KI crystals (*potassium iodide*) on a scoop.
- Add 100 mL of sample.
- Wait 2 minutes.
- Titrate with FAS (C) until the *red colour* is discharged.
- Record the volume of titrant used.

The mL of FAS titrant is equal to the mg/L Cl.

**Table A. 3:** List of suppliers for DBP standards.

| Target Analyte           |                           | CAS No.     | Catalogue No.   | Supplier             |
|--------------------------|---------------------------|-------------|-----------------|----------------------|
| <b>Trihalomethanes</b>   | Chloroform                | 67-66-3     |                 |                      |
|                          | Bromodichloromethane      | 75-27-4     | 48045           | Sigma-Aldrich, UK    |
|                          | Dibromochloromethane      | 124-48-1    | (EPA 551-A mix) |                      |
|                          | Bromoform                 | 75-25-2     |                 |                      |
| <b>Haloacetic acids</b>  | Monochloroacetic acid     | 79-11-8     |                 |                      |
|                          | Monobromoacetic acid      | 79-08-3     |                 |                      |
|                          | Dichloroacetic acid       | 79-43-6     |                 |                      |
|                          | Trichloroacetic acid      | 76-03-9     |                 |                      |
|                          | Bromochloroacetic acid    | 5589-96-8   | 49107-U         | Sigma-Aldrich, UK    |
|                          | Bromodichloroacetic acid  | 71133-14-7  | (EPA 552.3 mix) |                      |
|                          | Dibromoacetic acid        | 631-64-1    |                 |                      |
|                          | Dibromochloroacetic acid  | 5278-95-5   |                 |                      |
|                          | Tribromoacetic acid       | 75-96-7     |                 |                      |
| <b>Haloacetonitriles</b> | Dichloroacetonitrile      | 3018-12-0   |                 |                      |
|                          | Trichloroacetonitrile     | 545-06-2    |                 |                      |
|                          | Dibromoacetonitrile       | 3252-43-5   | 48046_EPA 551-B | Sigma-Aldrich, UK    |
|                          | Bromochloroacetonitrile   | 83463-62-1  |                 |                      |
|                          | Monochloroacetonitrile    | 107-14-2    | C19651          | Sigma-Aldrich, UK    |
|                          | Monobromoacetonitrile     | 590-17-0    | 242489          | Sigma-Aldrich, UK    |
|                          | Dibromochloroacetonitrile | 144772-39-4 | D425200         | Toronto Res. Chem.   |
| <b>Haloacetamides</b>    | Monochloroacetamide       | 79-07-2     | C0267           | Sigma-Aldrich, UK    |
|                          | Monobromoacetamide        | 683-57-8    | 301272          | Sigma-Aldrich, UK    |
|                          | Dichloroacetamide         | 683-72-7    | L00315          | Alfa Aesar, US       |
|                          | Trichloroacetamide        | 594-65-0    | L00411          | Alfa Aesar, US       |
|                          | Dibromoacetamide          | 598-70-9    | HAM006          | CanSyn Chem, Canada  |
|                          | Bromochloroacetamide      | 62872-34-8  | HAM001          | CanSyn Chem, Canada  |
|                          | Bromodichloroacetamide    | 98137-00-9  | HAM002          | CanSyn Chem, Canada  |
|                          | Dibromochloroacetamide    | 855878-13-6 | HAM005          | CanSyn Chem, Canada  |
|                          | Tribromoacetamide         | 594-47-8    | HAM003          | CanSyn. Chem, Canada |

**Table A. 4:** DBP monitoring in numbers (MDL, n° of samples, median concentrations).

| Target Analyte |                           | MDL<br>[µg/L] | Total samples<br>[n°] | Samples<br>>MDL [n°] | Median<br>concentration [µg/L] |
|----------------|---------------------------|---------------|-----------------------|----------------------|--------------------------------|
| <b>THMs</b>    | Chloroform                | 0.4           | 384                   | 384                  | 4.8                            |
|                | Bromodichloromethane      | 0.3           | 384                   | 384                  | 6.8                            |
|                | Dibromochloromethane      | 0.2           | 384                   | 384                  | 10.8                           |
|                | Bromoform                 | 0.4           | 384                   | 376                  | 7.7                            |
| <b>HAAs</b>    | Monochloroacetic acid     | 0.2           | 374                   | 320                  | 3.3                            |
|                | Monobromoacetic acid      | 0.5           | 374                   | 358                  | 1.4                            |
|                | Dichloroacetic acid       | 0.2           | 374                   | 324                  | 4.4                            |
|                | Trichloroacetic acid      | 0.2           | 374                   | 364                  | 0.9                            |
|                | Bromochloroacetic acid    | 0.1           | 374                   | 96                   | 2.6                            |
|                | Bromodichloroacetic acid  | 0.1           | 374                   | 340                  | 1.7                            |
|                | Dibromoacetic acid        | 0.7           | 374                   | 338                  | 2.5                            |
|                | Dibromochloroacetic acid  | 1             | 374                   | 338                  | 3.2                            |
|                | Tribromoacetic acid       | 1             | 374                   | 320                  | 2.9                            |
| <b>HANs</b>    | Dichloroacetonitrile      | 0.1           | 380                   | 308                  | 0.6                            |
|                | Trichloroacetonitrile     | 0.1           | 380                   | 302                  | 0.7                            |
|                | Dibromoacetonitrile       | 0.2           | 380                   | 266                  | 0.8                            |
|                | Bromochloroacetonitrile   | 0.2           | 380                   | 312                  | 0.6                            |
|                | Monochloroacetonitrile    | -             | 380                   | n/a                  | n/a                            |
|                | Monobromoacetonitrile     | 0.1           | 380                   | 82                   | 0.1                            |
|                | Dibromochloroacetonitrile | 0.5           | 380                   | 0                    | n/a                            |
| <b>HAcAms</b>  | Monochloroacetamide       | -             | 372                   | n/a                  | n/a                            |
|                | Monobromoacetamide        | 0.1           | 372                   | 244                  | 0.6                            |
|                | Dichloroacetamide         | 0.1           | 372                   | 368                  | 0.8                            |
|                | Trichloroacetamide        | 0.1           | 372                   | 260                  | 0.3                            |
|                | Dibromoacetamide          | 0.1           | 372                   | 350                  | 0.6                            |
|                | Bromochloroacetamide      | 0.1           | 372                   | 326                  | 0.8                            |
|                | Bromodichloroacetamide    | 0.1           | 372                   | 306                  | 0.3                            |
|                | Dibromochloroacetamide    | 0.1           | 372                   | 190                  | 0.3                            |
|                | Tribromoacetamide         | 0.1           | 372                   | 280                  | 0.3                            |

**Table A. 5:** List of suppliers for amide precursors.

| Name               | Formula                                             | CAS No.   | Catalogue No. | Supplier            |
|--------------------|-----------------------------------------------------|-----------|---------------|---------------------|
| Acetamide          | CH <sub>3</sub> CONH <sub>2</sub>                   | 60-35-5   | 00160         | Sigma Aldrich, UK   |
| Acetoacetamide     | CH <sub>3</sub> COCH <sub>2</sub> CONH <sub>2</sub> | 5977-14-0 | 328812        | Sigma Aldrich, UK   |
| Polyacrylamide     | (C <sub>3</sub> H <sub>5</sub> NO) <sub>n</sub>     | 9003-05-8 | 92560         | Sigma Aldrich, UK   |
| Acrylamide         | CH <sub>2</sub> =CHCONH <sub>2</sub>                | 79-06-1   | A9099         | Sigma Aldrich, UK   |
| β-Alaninamide      | C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> O      | 4726-85-6 | 8540850001    | Merck Millipore, UK |
| 4-Hydroxybenzamide | HOC <sub>6</sub> H <sub>4</sub> CONH <sub>2</sub>   | 619-57-8  | 270253        | Sigma Aldrich, UK   |

**Table A. 6:** List of suppliers for amide precursors.

Sodium phosphate *monobasic* monohydrate, NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, Mr = 137.99, CAS = 10049-21-5.

Sodium phosphate *dibasic* anhydrous, Na<sub>2</sub>HPO<sub>4</sub>, Mr = 141.96, CAS = 7558-79-4.

| pH  | Monobasic<br>[g/100 mL] | Dibasic<br>[g/100 mL] |
|-----|-------------------------|-----------------------|
| 6   | 12.972                  | 0.852                 |
| 7   | 8.459                   | 5.495                 |
| 7.5 | 4.609                   | 9.457                 |
| 8   | 1.891                   | 12.255                |
| 8.5 | 0.662                   | 13.518                |

## Appendix B. Database of actual and SDS tests in WTW A, B, C, D (4 Rounds)

**Table B. 1:** Raw data of **WTW A** (actual distribution samples & SDS tests) in **Round 1** (autumn 15'-14/09/2015).

|                      |                           |                      |      |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |      |     |
|----------------------|---------------------------|----------------------|------|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|---------------|----------|---------------|----------|------|-----|
| Date:                | 14/09/2015                |                      |      |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |      |     |
|                      | A                         |                      |      | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |               |          |               |          |      |     |
|                      | DBPs                      | Units                | MDL  | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          | 6-12 h                      |          | 24-48 h       |          | >72 h         |          |      |     |
|                      |                           |                      |      | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. | Concentration | std dev. | Concentration | std dev. |      |     |
| CHCl <sub>3</sub>    | Chloroform                | µg/L                 | 0.4  | 2.2                           | 0.1      | 3.0           | 0.2      | 4.8           | 0.1      | 5.2           | 0.1      | 6.3           | 0.2      | 8.6           | 0.1      |                             |          | 3.5           |          | 5.8           | 0.1      | 8.5  | 1.2 |
| CHBrCl <sub>2</sub>  | Bromodichloromethane      | µg/L                 | 0.3  | 3.2                           | 0.1      | 5.5           | 0.2      | 8.9           | 0.2      | 10.2          | 0.2      | 13.1          | 0.4      | 15.1          | 0.2      |                             |          | 6.2           |          | 11.0          | 0.2      | 15.7 | 2.1 |
| CHBr <sub>2</sub> Cl | Dibromochloromethane      | µg/L                 | 0.2  | 5.7                           | 0.2      | 7.3           | 0.3      | 14.4          | 0.4      | 18.5          | 0.4      | 21.3          | 0.9      | 22.4          | 0.3      |                             |          | 14.2          |          | 18.3          | 0.4      | 23.5 | 2.3 |
| CHBr <sub>3</sub>    | Bromoform                 | µg/L                 | 0.4  | 8.9                           | 0.1      | 11.0          | 0.1      | 15.0          | 1.0      | 15.9          | 0.8      | 16.8          | 1.0      | 17.0          | 0.2      |                             |          | 6.2           |          | 8.7           | 0.2      | 10.2 | 1.3 |
|                      | Total THMs                | µg/L                 |      | 20.0                          |          | 26.8          |          | 43.1          |          | 49.8          |          | 57.5          |          | 63.1          |          |                             |          | 30.1          |          | 43.7          |          | 57.9 |     |
| MCAA                 | Monochloroacetic acid     | µg/L                 | 0.2  | 3.3                           |          | 3.6           |          | 4.2           |          | 3.2           |          | 3.3           |          | -             |          |                             |          | -             |          | 3.6           |          | 3.8  |     |
| MBAA                 | Monobromoacetic acid      | µg/L                 | 0.5  | 29.3                          |          | 20.4          |          | 22.9          |          | 22.6          |          | 21.9          |          | -             |          |                             |          | -             |          | 22.3          |          | 21.2 |     |
| DCAA                 | Dichloroacetic acid       | µg/L                 | 0.2  | 2.8                           |          | 3.4           |          | 4.8           |          | 2.2           |          | 2.5           |          | -             |          |                             |          | -             |          | 2.1           |          | 2.2  |     |
| TCAA                 | Trichloroacetic acid      | µg/L                 | 0.2  | 8.0                           |          | 8.6           |          | 9.7           |          | 9.3           |          | 8.6           |          | -             |          |                             |          | -             |          | 8.6           |          | 8.4  |     |
| DBAA                 | Dibromoacetic acid        | µg/L                 | 0.1  | 6.1                           |          | 8.4           |          | 9.8           |          | 8.8           |          | 8.1           |          | -             |          |                             |          | -             |          | 8.3           |          | 7.4  |     |
| BCAA                 | Bromochloroacetic acid    | µg/L                 | 0.1  | 5.0                           |          | nd            |          | 4.7           |          | nd            |          | 4.7           |          | -             |          |                             |          | -             |          | 10.4          |          | nd   |     |
| BDCAA                | Bromodichloroacetic acid  | µg/L                 | 0.7  | <0.7                          |          | <0.7          |          | <0.7          |          | <0.7          |          | 4.1           |          | -             |          |                             |          | -             |          | 4.6           |          | 4.1  |     |
| DBCAA                | Dibromochloroacetic acid  | µg/L                 | 1    | <1                            |          | <1            |          | <1            |          | <1            |          | 1.7           |          | -             |          |                             |          | -             |          | 3.5           |          | 3.2  |     |
| TBAA                 | Tribrromoacetic acid      | µg/L                 | 1    | <1                            |          | <1            |          | <1            |          | <1            |          | <1            |          | -             |          |                             |          | -             |          | 3.3           |          | 1.4  |     |
|                      | Total HAAs                | µg/L                 |      | 49.5                          |          | 44.3          |          | 56.0          |          | 46.0          |          | 55.0          |          |               |          |                             |          |               |          | 66.9          |          | 51.7 |     |
| MCAN                 | Monochloroacetonitrile    | µg/L                 | -    | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |                             |          | -             |          | nd            | -        | nd   | -   |
| MBAN                 | Monobromoacetonitrile     | µg/L                 | 0.1  | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |                             |          | -             |          | nd            | -        | nd   | -   |
| DCAN                 | Dichloroacetonitrile      | µg/L                 | 0.01 | <0.1                          | -        | <0.1          | -        | 0.0           | 0.0      | 0.1           | 0.0      | 0.1           | 0.0      | 0.1           | 0.0      |                             |          | -             |          | 1.2           | 0.0      | 0.5  | 0.1 |
| TCAN                 | Trichloroacetonitrile     | µg/L                 | 0.01 | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        |                             |          | -             |          | 1.8           | -        | <0.1 | -   |
| DBAN                 | Dibromoacetonitrile       | µg/L                 | 0.02 | 2.8                           | 0.0      | 2.9           | 0.1      | 3.0           | 0.0      | 3.4           | 0.0      | 2.8           | 0.1      | 3.3           | 0.0      |                             |          | -             |          | 2.7           | 0.2      | 2.9  | 0.2 |
| BCAN                 | Bromochloroacetonitrile   | µg/L                 | 0.02 | 0.2                           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.6           | 0.0      | 0.4           | 0.1      | 0.5           | 0.0      |                             |          | -             |          | 0.4           | 0.0      | 0.5  | 0.0 |
| DBCAN                | Dibromochloroacetonitrile | µg/L                 | 0.5  | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |                             |          | -             |          | nd            | -        | nd   | -   |
|                      | Total HANs                | µg/L                 |      | 3.1                           |          | 3.3           |          | 3.4           |          | 4.1           |          | 3.3           |          | 3.8           |          |                             |          |               |          | 6.1           |          | 3.9  |     |
| MCaAcAm              | Monochloroacetamide       | µg/L                 | -    | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |                             |          | -             |          | nd            | -        | nd   | -   |
| MBaAcAm              | Monobromoacetamide        | µg/L                 | 0.1  | 0.1                           | 0.0      | 0.2           | 0.0      | 0.2           | 0.1      | 0.2           | 0.2      | 0.1           | 0.1      | 0.1           | 0.0      |                             |          | -             |          | 0.6           | 0.1      | 1.0  | 0.2 |
| DCAcAm               | Dichloroacetamide         | µg/L                 | 0.1  | 0.7                           | 0.0      | 0.8           | 0.1      | 0.8           | 0.1      | 0.3           | 0.0      | <0.1          | -        | <0.1          | -        |                             |          | -             |          | 1.4           | 0.0      | 1.4  | 0.2 |
| TCAcAm               | Trichloroacetamide        | µg/L                 | 0.1  | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        |                             |          | -             |          | <0.1          | -        | <0.1 | -   |
| DBAcAm               | Dibromoacetamide          | µg/L                 | 0.1  | 0.3                           | 0.0      | 0.4           | 0.0      | 0.4           | 0.1      | 0.3           | 0.0      | 0.2           | 0.0      | 0.6           | 0.0      |                             |          | -             |          | 0.4           | 0.1      | 0.4  | 0.0 |
| BCAcAm               | Bromochloroacetamide      | µg/L                 | 0.1  | 0.7                           | 0.1      | 1.3           | 0.1      | 1.1           | 0.2      | 0.8           | 0.1      | 0.8           | 0.1      | 0.9           | 0.1      |                             |          | -             |          | 0.5           | 0.1      | 1.1  | 0.2 |
| BDCAcAm              | Bromodichloroacetamide    | µg/L                 | 0.1  | 0.4                           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      |                             |          | -             |          | 0.5           | 0.0      | 0.6  | 0.1 |
| DBCACAm              | Dibromochloroacetamide    | µg/L                 | 0.1  | 0.6                           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      |                             |          | -             |          | 0.7           | 0.0      | 0.8  | 0.1 |
| TBAcAm               | Tribrromoacetamide        | µg/L                 | 0.1  | 0.5                           | 0.1      | 0.4           | 0.1      | 0.2           | 0.1      | 0.2           | 0.1      | 0.2           | 0.0      | 0.3           | 0.1      |                             |          | -             |          | 0.2           | 0.0      | 0.3  | 0.0 |
|                      | Total HAcs                | µg/L                 | 0.1  | 3.2                           |          | 4.0           |          | 3.6           |          | 2.8           |          | 2.3           |          | 2.9           |          |                             |          |               |          | 4.3           |          | 5.4  |     |
| NDMA                 | N-nitrosodimethylamine    | ng/L                 | 0.1  | -                             |          | -             |          | -             |          | -             |          | -             |          | -             |          |                             |          | 0.12          |          | 0.19          |          | 0.21 |     |
|                      | Quality parameters        |                      |      |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |      |     |
|                      | TOC                       | mg/L C               |      | 3.17                          |          | 3.23          |          | 3.18          |          | 3.67          |          | 3.10          |          | 3.41          |          |                             |          | 3.06          |          | -             |          | -    |     |
|                      | Temperature               | °C                   |      | 17.2                          |          | 17.2          |          | 17.2          |          | 17.2          |          | 17.2          |          | 17.2          |          |                             |          | 17.2          |          | 17.0          |          | 16.9 |     |
|                      | Chlorine residual         | mg/L Cl <sup>2</sup> |      | -                             |          | -             |          | -             |          | -             |          | -             |          | 0.2           |          |                             |          |               |          | 0.6           |          | 0.1  |     |
|                      | Bromate                   | µg/L                 |      | -                             |          | -             |          | -             |          | -             |          | -             |          | -             |          |                             |          | 0.39          |          | -             |          | -    |     |

| Date:                | 08/02/2016               |       |     | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |               |          |               |          |
|----------------------|--------------------------|-------|-----|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|---------------|----------|---------------|----------|
|                      | A                        |       |     | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          | 6-12 h                      |          | 24-48 h       |          | >72 h         |          |
|                      | DBPs                     | Units | MDL | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. | Concentration | std dev. | Concentration | std dev. |
| CHCl <sub>3</sub>    | Chloroform               |       |     | 2.0                           | 0.0      | 2.6           | 0.0      | 3.3           | 0.0      | 5.3           | 0.0      | 6.0           | 0.0      | 7.9           | 0.0      | 2.8                         | 0.0      | 4.6           | 0.0      | 8.2           | 0.0      |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L  | 0.4 | 2.9                           | 0.0      | 4.2           | 0.0      | 7.5           | 0.0      | 9.9           | 0.0      | 10.6          | 0.0      | 13.6          | 0.0      | 4.9                         | 0.0      | 7.4           | 0.0      | 11.2          | 0.0      |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L  | 0.3 | 8.6                           | 0.0      | 9.1           | 0.1      | 9.5           | 0.1      | 15.4          | 0.1      | 17.8          | 0.2      | 22.4          | 0.2      | 12.4                        | 0.0      | 16.4          | 0.0      | 18.1          | 0.1      |
| CHBr <sub>3</sub>    | Bromoform                | µg/L  | 0.2 | 6.0                           | 0.1      | 8.1           | 0.1      | 9.2           | 0.0      | 13.2          | 0.1      | 15.3          | 0.1      | 16.1          | 0.1      | 5.5                         | 0.0      | 7.6           | 0.0      | 15.4          | 0.1      |
|                      | Total THMs               | µg/L  | 0.4 | 19.5                          |          | 24.0          |          | 29.5          |          | 43.8          |          | 49.7          |          | 60.0          |          | 25.6                        |          | 36.0          |          | 52.9          |          |
|                      |                          | µg/L  |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |
| MCAA                 | Monochloroacetic acid    | µg/L  | 0.2 | 3.9                           | 0.2      | 3.6           | 0.2      | 4.1           | 0.1      | nd            | -        | 3.2           | 0.1      | 3.0           | 0.1      | 3.7                         | 0.2      | 5.1           | 0.3      | 4.1           | 0.1      |
| MBAA                 | Monobromoacetic acid     | µg/L  | 0.5 | 0.5                           | 0.0      | 0.5           | 0.0      | 0.5           | 0.0      | 0.5           | 0.0      | 0.8           | 0.0      | 0.7           | 0.0      | 0.5                         | 0.0      | 0.6           | 0.0      | 0.9           | 0.0      |
| DCAA                 | Dichloroacetic acid      | µg/L  | 0.2 | 0.7                           | 0.0      | 0.9           | 0.2      | 1.4           | 0.2      | nd            | -        | 1.1           | 0        | 1.2           | 0.1      | 0.8                         | 0.0      | 0.9           | 0.0      | 1.1           | 0.0      |
| TCAA                 | Trichloroacetic acid     | µg/L  | 0.2 | 1.0                           | 0.0      | 0.9           | 0.0      | 1.0           | 0.0      | 0.9           | 0.0      | 1.0           | 0.0      | 1.0           | 0.0      | 1.0                         | 0.1      | 1.3           | 0.1      | 1.3           | 0.0      |
| DBAA                 | Dibromoacetic acid       | µg/L  | 0.1 | 1.6                           | 0.0      | 1.5           | 0.0      | 1.6           | 0.1      | 1.1           | 0.0      | 1.8           | 0.0      | 1.8           | 0.0      | 1.8                         | 0.1      | 1.7           | 0.0      | 1.9           | 0.0      |
| BCAA                 | Bromochloroacetic acid   | µg/L  | 0.1 | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |
| BDCAA                | Bromodichloroacetic acid | µg/L  | 0.7 | 1.1                           | 0.0      | 1.2           | 0.0      | 1.3           | 0.0      | 1.3           | 0.0      | 1.2           | 0.0      | 1.2           | 0.0      | 1.6                         | 0.0      | 2.2           | 0.2      | 1.9           | 0.1      |
| DBCAA                | Dibromochloroacetic acid | µg/L  | 1   | 1.3                           | 0.0      | 2.4           | 0.0      | 1             | 0.0      | 1.1           | 0.0      | 1.6           | 0.0      | 1.8           | 0.0      | 1.4                         | 0.0      | <1            | -        | 1.0           | 0.0      |
| TBAA                 | Tribrmoacetic acid       | µg/L  | 1   | 1.5                           | 0.0      | 1.1           | 0.0      | 1.6           | 0.0      | <1            | 0.0      | 2.4           | 0.0      | 1.4           | 0.0      | 3.5                         | 0.1      | 1.8           | 0.0      | 2.8           | 0        |
|                      | Total HAAs               | µg/L  |     | 11.6                          |          | 12.0          |          | 12.5          |          | 4.9           |          | 13.2          |          | 12.2          |          | 14.3                        |          | 13.6          |          | 15.0          |          |
|                      |                          |       |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |
| MCAN                 | Monochloroacetnitrile    | µg/L  | -   | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |
| MBAN                 | Monobromoacetnitrile     | µg/L  | 0.1 | <0.1                          | -        | <0.1          | -        | <0.1          | -        | 0.2           | 0.0      | 0.1           | 0.0      | 0.1           | 0.0      | <0.1                        | -        | 0.1           | 0.0      | 0.1           | 0.0      |
| DCAN                 | Dichloroacetnitrile      | µg/L  | 0.1 | <0.1                          | -        | 0.1           | 0.0      | 0.2           | 0.0      | 0.5           | 0.0      | 0.7           | 0.0      | 0.6           | 0.0      | <0.1                        | -        | <0.1          | -        | <0.1          | -        |
| TCAN                 | Trichloroacetnitrile     | µg/L  | 0.1 | 0.7                           | 0.0      | 0.7           | 0.0      | 0.7           | 0.0      | 0.7           | 0.0      | 0.8           | 0.0      | 0.8           | 0.0      | 0.7                         | 0.0      | 0.7           | 0.0      | 0.7           | 0.0      |
| DBAN                 | Dibromoacetnitrile       | µg/L  | 0.2 | 1.1                           | 0.0      | 1.7           | 0.1      | 3.1           | 0.1      | 1.4           | 0.1      | 3.4           | 0.1      | 3.5           | 0.1      | 2.0                         | 0.2      | 3.3           | 0.1      | 3.7           | 0.1      |
| BCAN                 | Bromochloroacetnitrile   | µg/L  | 0.5 | 0.8                           | 0.1      | 0.9           | 0.0      | 1.7           | 0.1      | 1.1           | 0.0      |               |          |               |          |                             |          |               |          |               |          |

**Table B. 3:** Raw data of **WTW A** (actual distribution samples & SDS tests) in **Round 3** (spring 16<sup>th</sup>-09/05/2016).

|                      |                           |                        |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |  |
|----------------------|---------------------------|------------------------|-----|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|---------------|----------|---------------|----------|--|
| Date:                | 09/05/2016                |                        |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |  |
|                      | A                         |                        |     | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |               |          |               |          |  |
|                      |                           |                        |     | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          | 6-12 h                      |          | 24-48 h       |          | >72 h         |          |  |
|                      | DBPs                      | Units                  | MDL | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. | Concentration | std dev. | Concentration | std dev. |  |
| CHCl <sub>3</sub>    | Chloroform                | µg/L                   |     | 4.3                           | 0.1      | 7.0           | 0.5      | 8.3           | 0.2      | 9.3           | 0.2      | 10.6          | 0.3      | 11.8          | 0.0      | 4.9                         | 0.3      | 7.5           | 0.1      | 11.9          | 1.0      |  |
| CHBrCl <sub>2</sub>  | Bromodichloromethane      | µg/L                   | 0.4 | 5.8                           | 0.1      | 6.2           | 0.2      | 7.1           | 0.2      | 9.4           | 0.5      | 13.0          | 0.4      | 15.0          | 0.6      | 6.1                         | 0.3      | 9.8           | 0.7      | 15.6          | 1.0      |  |
| CHBr <sub>2</sub> Cl | Dibromochloromethane      | µg/L                   | 0.3 | 13.5                          | 0.3      | 14.6          | 0.0      | 18.6          | 0.7      | 19.3          | 2.1      | 19.5          | 0.1      | 20.3          | 0.4      | 12.0                        | 0.2      | 19.0          | 0.6      | 21.0          | 0.9      |  |
| CHBr <sub>3</sub>    | Bromoform                 | µg/L                   | 0.2 | 4.8                           | 0.5      | 5.7           | 0.5      | 6.0           | 0.3      | 8.9           | 0.3      | 10.4          | 0.5      | 13.2          | 0.7      | 6.0                         | 0.5      | 8.9           | 0.6      | 12.3          | 0.3      |  |
|                      | Total THMs                |                        | 0.4 | 28.3                          |          | 33.6          |          | 40.0          |          | 46.9          |          | 53.5          |          | 60.3          |          | 29.0                        |          | 45.2          |          | 60.8          |          |  |
| MCAA                 | Monochloroacetic acid     | µg/L                   |     | 4.0                           | 0.2      | 3.5           | 0.5      | 3.8           | 0.1      | 3.0           | 0.1      | 2.4           | 0.2      | 3.5           | 0.3      | 3.9                         | 0.3      | 3.4           | 0.6      | 3.4           | 0.3      |  |
| MBAA                 | Monobromoacetic acid      | µg/L                   | 0.2 | 1.0                           | 0.2      | 1.1           | 0.6      | 1.2           | 0.5      | 1.6           | 0.1      | 0.4           | 0.0      | 1.1           | 0.1      | 1.6                         | 0.0      | 1.9           | 0.1      | 1.3           | 0.1      |  |
| DCAA                 | Dichloroacetic acid       | µg/L                   | 0.5 | 11.2                          | 0.1      | 13.4          | 0.2      | 17.3          | 0.0      | 10.5          | 0.1      | 6.6           | 0.1      | 10.6          | 0.1      | 13.2                        | 0.4      | 15.7          | 0.3      | 11.1          | 1.5      |  |
| TCAA                 | Trichloroacetic acid      | µg/L                   | 0.2 | 1.0                           | 0.1      | 0.7           | 0.1      | 0.6           | 0.2      | 0.6           | 0.0      | 0.7           | 0.1      | 0.6           | 0.0      | 0.8                         | 0.1      | 0.6           | 0.1      | 0.7           | 0.0      |  |
| DBAA                 | Dibromoacetic acid        | µg/L                   | 0.2 | 5.9                           | 0.3      | 8.9           | 0.2      | 8.7           | 0.1      | 8.8           | 0.4      | 10.5          | 0.2      | 8.5           | 0.0      | 8.0                         | 0.4      | 8.7           | 0.4      | 7.6           | 0.6      |  |
| BCAA                 | Bromochloroacetic acid    | µg/L                   | 0.1 | 0.2                           | 0.0      | 0.1           | 0.0      | nd            | -        | nd            | -        | nd            | -        | 0.1           | 0.0      | 0.7                         | 0.0      | 0.2           | 0.0      | 0.5           | 0.0      |  |
| BDCAA                | Bromodichloroacetic acid  | µg/L                   | 0.1 | 4.7                           | 0.1      | 5.0           | 0.0      | 5.2           | 0.5      | 5.4           | 0.1      | 3.9           | 0.0      | 6.3           | 0.2      | 3.7                         | 0.3      | 4.8           | 0.2      | 6.0           | 1.1      |  |
| DBCAA                | Dibromochloroacetic acid  | µg/L                   | 0.7 | 5.9                           | 0.3      | 8.9           | 0.2      | 8.7           | 0.1      | 8.8           | 0.4      | 10.5          | 0.2      | 8.5           | 0.1      | 9.1                         | 0.3      | 6.6           | 0.8      | 8.3           | 0.6      |  |
| TBAA                 | Trihaloacetic acid        | µg/L                   | 1   | 1.5                           | 0.2      | 2.6           | 0.4      | 2.3           | 0.5      | 3.1           | 0.1      | 4.4           | 0.0      | 1.2           | 0.1      | 3.4                         | 0.2      | 2.8           | 0.2      | 2.7           | 0.8      |  |
|                      | Total HAAs                |                        | 1   | 35.2                          |          | 44.3          |          | 47.8          |          | 41.8          |          | 39.5          |          | 40.1          |          | 43.7                        |          | 44.4          |          | 41.1          |          |  |
| MCAN                 | Monochloroacetonitrile    | µg/L                   |     | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |  |
| MBAN                 | Monobromoacetonitrile     | µg/L                   | -   | 0.6                           | 0.2      | 0.4           | 0.1      | 0.3           | 0.1      | 0.6           | 0.0      | 0.2           | 0.0      | 0.2           | 0.0      | 0.2                         | 0.0      | 0.5           | 0.1      | 0.5           | 0.1      |  |
| DCAN                 | Dichloroacetonitrile      | µg/L                   | 0.1 | 0.4                           | 0.0      | 0.5           | 0.1      | 0.6           | 0.1      | 0.9           | 0.0      | 0.7           | 0.0      | 0.7           | 0.0      | 0.4                         | 0.1      | 0.5           | 0.0      | 0.7           | 0.1      |  |
| TCAN                 | Trichloroacetonitrile     | µg/L                   | 0.1 | 0.4                           | 0.0      | 0.4           | 0.1      | 0.4           | 0.0      | 0.6           | 0.0      | 0.6           | 0.1      | 0.8           | 0.0      | 0.3                         | 0.1      | 0.7           | 0.0      | 1.0           | 0.0      |  |
| DBAN                 | Dibromoacetonitrile       | µg/L                   | 0.1 | 1.6                           | 0.1      | 2.1           | -        | 1.2           | 0.0      | 0.4           | 0.0      | <0.2          | -        | 1.0           | 0.0      | 1.4                         | 0.0      | 0.4           | 0.1      | 1.1           | 0.0      |  |
| BCAN                 | Bromochloroacetonitrile   | µg/L                   | 0.2 | 0.9                           | 0.1      | 0.9           | 0.2      | 1.2           | 0.0      | 1.4           | 0.1      | nd            | -        | 1.3           | 0.0      | 1.7                         | 0.4      | 1.5           | 0.1      | 1.3           | 0.4      |  |
| DBCAN                | Dibromochloroacetonitrile | µg/L                   | 0.2 | <0.5                          | -        | <0.5          | -        | <0.5          | -        | <0.5          | -        | <0.5          | -        | <0.5          | -        | nd                          | -        | nd            | -        | nd            | -        |  |
|                      | Total HANs                |                        | 0.5 | 3.9                           |          | 4.3           |          | 3.7           |          | 3.9           |          | 1.5           |          | 4.0           |          | 4.1                         |          | 3.7           |          | 4.7           |          |  |
| MCAcAm               | Monochloroacetamide       | µg/L                   |     | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |  |
| MBAcAm               | Monobromoacetamide        | µg/L                   | -   | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        | <0.1          | -        | <0.1          | -        |  |
| DCAcAm               | Dichloroacetamide         | µg/L                   | 0.1 | 1.4                           | 0.1      | 1.8           | 0.2      | 0.6           | 0.2      | 0.5           | 0.0      | 0.7           | 0.0      | 1.0           | 0.0      | 1.0                         | 0.0      | 0.8           | 0.1      | 0.9           | 0.0      |  |
| TCAcAm               | Trichloroacetamide        | µg/L                   | 0.1 | 0.3                           | 0.0      | 0.3           | 0.1      | 0.1           | 0.0      | 0.1           | 0.0      | 0.1           | 0.0      | 0.2           | 0.0      | 0.2                         | 0.0      | 0.1           | 0.0      | 0.2           | 0.0      |  |
| DBAcAm               | Dibromoacetamide          | µg/L                   | 0.1 | 0.7                           | 0.0      | 0.5           | 0.1      | 0.4           | 0.0      | 0.4           | 0.0      | 0.8           | 0.0      | 0.6           | 0.0      | 0.3                         | 0.0      | 0.4           | 0.0      | 0.8           | 0.0      |  |
| BCAcAm               | Bromochloroacetamide      | µg/L                   | 0.1 | 0.9                           | 0.1      | 0.8           | 0.1      | 1.0           | 0.0      | 1.1           | 0.1      | 1.1           | 0.1      | 1.6           | 0.1      | 0.8                         | 0.1      | 0.9           | 0.0      | 1.0           | 0.0      |  |
| BDCAcAm              | Bromodichloroacetamide    | µg/L                   | 0.1 | 0.5                           | 0.1      | 0.4           | 0.0      | 0.5           | 0.1      | 0.6           | 0.1      | 0.5           | 0.0      | 0.6           | 0.0      | 0.2                         | 0.0      | 0.3           | 0.0      | 0.5           | 0.0      |  |
| DBCAcAm              | Dibromochloroacetamide    | µg/L                   | 0.1 | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        | <0.1          | -        | <0.1          | -        |  |
| TBAcAm               | Trihaloacetamide          | µg/L                   | 0.1 | 0.5                           | 0.0      | 0.7           | 0.1      | 0.6           | 0.2      | 0.4           | 0.0      | <0.1          | -        | <0.1          | -        | 0.3                         | 0.1      | 0.2           | 0.0      | 0.1           | 0.0      |  |
|                      | Total HAcAms              |                        | 0.1 | 4.2                           |          | 4.4           |          | 3.2           |          | 3.0           |          | 3.3           |          | 4.1           |          | 2.5                         |          | 2.7           |          | 3.4           |          |  |
| NDMA                 | N-nitrosodimethylamine    | ng/L                   | 0.1 | -                             |          | -             |          | -             |          | -             |          | -             |          | -             |          | 0.62                        |          | 0.32          |          | 0.23          |          |  |
|                      | Quality parameters        |                        |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |  |
|                      | TOC                       | mg/L C                 |     | 3.39                          |          | 3.30          |          | 3.32          |          | 3.40          |          | 3.49          |          | 3.41          |          | 3.55                        |          | 3.45          |          | 3.3           |          |  |
|                      | Temperature               | °C                     |     | 14.0                          |          | 14.0          |          | 14.0          |          | 14.0          |          | 14.0          |          | 14.0          |          | 14.0                        |          | 14.0          |          | 14.0          |          |  |
|                      | Chlorine residual         | mg/L Cl <sup>-</sup> 2 |     | 0.5                           |          | 0.4           |          | 0.2           |          | 0.2           |          | 0.2           |          | 0.1           |          | 1.0                         |          | 0.3           |          | 0.2           |          |  |
|                      | pH                        |                        |     | 7.0                           |          | 7.2           |          | 7.4           |          | 7.7           |          | 7.0           |          | 7.5           |          | 7.5                         |          | 7.4           |          | 7.4           |          |  |
|                      | UVAbs                     |                        |     | 0.064                         |          | 0.048         |          | 0.045         |          | 0.043         |          | 0.043         |          | 0.043         |          | 0.063                       |          | 0.062         |          | 0.061         |          |  |
|                      | SUVA                      |                        |     | 1.9                           |          | 1.5           |          | 1.4           |          | 1.3           |          | 1.2           |          | 1.3           |          | 1.8                         |          | 1.8           |          | 1.8           |          |  |
|                      | Bromide                   | µg/L                   |     |                               |          |               |          |               |          |               |          |               |          |               |          | <12                         |          |               |          |               |          |  |

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| Date:                         | 14/09/2015                 |       |     |               |          |               |          |               |          |               |          |               |          |               |          |
|-------------------------------|----------------------------|-------|-----|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|
| B                             |                            |       |     |               |          |               |          |               |          |               |          |               |          |               |          |
| Simulation Distribution Tests |                            |       |     |               |          |               |          |               |          |               |          |               |          |               |          |
|                               |                            |       |     | 6 h           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          |
|                               |                            | Units | MDL | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. |
| DBPs                          |                            |       |     |               |          |               |          |               |          |               |          |               |          |               |          |
| CHCl <sub>3</sub>             | Chloroform                 | µg/L  | 0.4 | 1.4           | 0.1      | 1.5           | 0.1      | 3.0           | 0.0      | 3.8           | 0.0      | 3.9           | 0.1      | 4.1           | 0.1      |
| CHBrCl <sub>2</sub>           | Bromodichloromethane       | µg/L  | 0.3 | 0.4           | 0.1      | 0.5           | 0.0      | 4.5           | 0.0      | 5.6           | 0.1      | 5.9           | 0.2      | 6.0           | 0.2      |
| CHBr <sub>2</sub> Cl          | Dibromochloromethane       | µg/L  | 0.2 | 3.3           | 0.0      | 4.0           | 0.0      | 5.3           | 0.2      | 7.2           | 0.2      | 15.9          | 0.3      | 15.0          | 0.3      |
| CHBr <sub>3</sub>             | Bromoform                  | µg/L  | 0.4 | 9.1           | 0.4      | 10.9          | 0.0      | 13.4          | 0.0      | 18.0          | 0.1      | 20.0          | 0.7      | 31.5          | 0.2      |
| Total THMs                    |                            | µg/L  |     | 14.1          |          | 16.9          |          | 26.2          |          | 34.6          |          | 45.7          |          | 56.6          |          |
| MCAA                          | Monochloroacetic acid      | µg/L  | 0.2 | 3.2           |          | 3.3           |          | 3.2           |          | 3.1           |          | 3.3           |          | -             |          |
| MBAA                          | Monobromoacetic acid       | µg/L  | 0.5 | 23.8          |          | 23.2          |          | 20.2          |          | 20.0          |          | 20.3          |          | -             |          |
| DCAA                          | Dichloroacetic acid        | µg/L  | 0.2 | 2.5           |          | 2.8           |          | 2.3           |          | 2.1           |          | 2.5           |          | -             |          |
| TCAA                          | Trichloroacetic acid       | µg/L  | 0.2 | 9.1           |          | 8.9           |          | <0.2          |          | 8.2           |          | 8.2           |          | -             |          |
| DBAA                          | Dibromoacetic acid         | µg/L  | 0.1 | 8.5           |          | 8.5           |          | 7.8           |          | 8.1           |          | 8.2           |          | -             |          |
| BCAA                          | Bromochloroacetic acid     | µg/L  | 0.1 | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | -             |          |
| BDCAA                         | Bromodichloroacetic acid   | µg/L  | 0.7 | 4.6           |          | 4.6           |          | 4.3           |          | 4.5           |          | 4.5           |          | -             |          |
| DBCAs                         | Dibromochloroacetic acid   | µg/L  | 1   | 3.3           |          | 3.4           |          | 3.2           |          | 3.6           |          | 3.5           |          | -             |          |
| TBAAs                         | Trihaloacetic acid         | µg/L  | 1   | 2.4           |          | 2.8           |          | 3.1           |          | 4.6           |          | 4             |          | -             |          |
| Total HAAs                    |                            | µg/L  |     | 57.5          |          | 57.6          |          | 44.1          |          | 54.3          |          | 54.6          |          |               |          |
| MCAN                          | Monochloroacetoneitrile    | µg/L  | -   | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | -             | -        |
| MBAN                          | Monobromoacetoneitrile     | µg/L  | 0.1 | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | -             | -        |
| DCAN                          | Dichloroacetoneitrile      | µg/L  | 0.1 | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        |
| TCAN                          | Trichloroacetoneitrile     | µg/L  | 0.1 | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | -             | -        |
| DBAN                          | Dibromoacetoneitrile       | µg/L  | 0.2 | 2.0           | 0.0      | 2.1           | 0.1      | 2.3           | 0.1      | 2.4           | 0.0      | 2.1           | 0.0      | 2.5           | 0.0      |
| BCAN                          | Bromochloroacetoneitrile   | µg/L  | 0.2 | <0.2          | -        | <0.2          | -        | 0.1           | 0.0      | 0.1           | 0.0      | 0.1           | 0.0      | 0.1           | 0.0      |
| DBCAN                         | Dibromochloroacetoneitrile | µg/L  | 0.5 | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |
| Total HANs                    |                            | µg/L  |     | 2.0           |          | 2.1           |          | 2.4           |          | 2.5           |          | 2.2           |          | 2.6           |          |
| MCACAm                        | Monochloroacetamide        | µg/L  | -   | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |
| MBACAm                        | Monobromoacetamide         | µg/L  | 0.1 | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | 0.1           | 0.1      |
| DCACAm                        | Dichloroacetamide          | µg/L  | 0.1 | 1.1           | 0.0      | 1.0           | 0.0      | 0.8           | 0.1      | 0.8           | 0.0      | 0.2           | 0.0      | 0.3           | 0.0      |
| TCACAm                        | Trichloroacetamide         | µg/L  | 0.1 | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        |
| DBACAm                        | Dibromoacetamide           | µg/L  | 0.1 | 0.4           | 0.1      | 0.6           | 0.1      | 0.2           | 0.0      | 0.3           | 0.1      | 0.2           | 0.1      | 0.2           | 0.0      |
| BCACAm                        | Bromochloroacetamide       | µg/L  | 0.1 | 0.4           | 0.0      | 0.3           | 0.0      | 0.6           | 0.1      | 0.8           | 0.1      | 0.8           | 0.1      | 0.9           | 0.2      |
| BDCACAm                       | Bromodichloroacetamide     | µg/L  | 0.1 | 0.4           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      |
| DBCACAm                       | Dibromochloroacetamide     | µg/L  | 0.1 | 0.6           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      |
| TBACAm                        | Trihaloacetamide           | µg/L  | 0.1 | 0.5           | 0.1      | 0.7           | 0.1      | 0.3           | 0.1      |               |          |               |          |               |          |

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**Table B. 7:** Raw data of **WTW B** (actual distribution samples & SDS tests) in **Round 3** (spring 16<sup>3</sup>-09/05/2016).

|         |                           |                      |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |  |
|---------|---------------------------|----------------------|-----|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|---------------|----------|---------------|----------|--|
| Date:   | 09/05/2016                |                      |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |  |
|         | B                         |                      |     | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |               |          |               |          |  |
|         |                           |                      |     | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          | 6-12 h                      |          | 24-48 h       |          | 72-106 h      |          |  |
|         | DBPs                      | Units                | MDL | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. | Concentration | std dev. | Concentration | std dev. |  |
| CHCB    | Chloroform                | µg/L                 | 0.4 | 4.4                           | 0.0      | 6.8           | 0.7      | 8.4           | 0.2      | 8.7           | 0.5      | 9.1           | 0.2      | 9.2           | 0.3      | 4.9                         | 0.3      | 8.5           | 0.2      | 10.1          | 0.5      |  |
| CHBrCl2 | Bromodichloromethane      | µg/L                 | 0.3 | 1.0                           | 0.1      | 2.8           | 0.0      | 4.4           | 0.0      | 5.1           | 0.0      | 6.5           | 0.3      | 8.4           | 0.0      | 3.6                         | 0.1      | 5.9           | 0.0      | 7.7           | 0.0      |  |
| CHBr2Cl | Dibromochloromethane      | µg/L                 | 0.2 | 6.5                           | 0.2      | 8.0           | 0.3      | 9.6           | 0.5      | 10.6          | 0.4      | 15.6          | 0.4      | 17.1          | 0.4      | 9.8                         | 0.9      | 12.3          | 0.1      | 17.4          | 0.0      |  |
| CHBr3   | Bromoform                 | µg/L                 | 0.4 | 6.3                           | 0.1      | 6.5           | 0.1      | 7.6           | 0.2      | 8.4           | 0.3      | 11.7          | 0.0      | 16.4          | 0.8      | 8.1                         | 0.4      | 12.6          | 0.0      | 18.4          | 0.0      |  |
|         | Total THMs                | µg/L                 |     | 18.3                          |          | 24.1          |          | 30.0          |          | 32.8          |          | 43.0          |          | 51.2          |          | 26.4                        |          | 39.3          |          | 53.6          |          |  |
| MCAA    | Monochloroacetic acid     | µg/L                 | 0.2 | 3.3                           | 0.4      | 3.8           | 0.0      | 4.5           | 0.6      | 4.9           | 0.5      | 4.4           | 0.0      | 3.6           | 0.6      | 3.2                         | 0.0      | 5.1           | 0.1      | 4.0           | 0.1      |  |
| MBAA    | Monobromoacetic acid      | µg/L                 | 0.5 | 0.6                           | 0.2      | 0.6           | 0.2      | 0.6           | 0.3      | 0.6           | 0.1      | 0.8           | 0.1      | 0.8           | 0.1      | 0.5                         | 0.0      | 0.6           | 0.1      | 1.0           | 0.0      |  |
| DCAA    | Dichloroacetic acid       | µg/L                 | 0.2 | 9.9                           | 1.2      | 11.1          | 0.6      | 7.1           | 0.5      | 7.7           | 0.9      | 11.2          | 0.0      | 16.9          | 0.0      | 10.6                        | 0.0      | 7.5           | 0.1      | 10.3          | 0.0      |  |
| TCAA    | Trichloroacetic acid      | µg/L                 | 0.2 | <0.2                          | -        | <0.2          | -        | <0.2          | -        | 0.2           | 0.0      | 0.2           | 0.0      | 0.2           | 0.0      | <0.2                        | -        | 0.2           | 0.0      | 0.2           | 0.0      |  |
| DBAA    | Dibromoacetic acid        | µg/L                 | 0.1 | 5.7                           | 0.8      | 7.3           | 0.0      | 5.1           | 0.1      | 5.0           | 0.4      | 5.7           | 0.1      | 7.2           | 0.0      | 5.8                         | 0.0      | 6.5           | 0.0      | 8.8           | 0.0      |  |
| BCAA    | Bromochloroacetic acid    | µg/L                 | 0.1 | nd                            | -        | 0.1           | 0.0      | 0.2           | 0.0      | nd            | -        | nd            | -        | 0.2           | 0.0      | nd                          | -        | 0.1           | 0.0      | nd            | -        |  |
| BDCAA   | Bromodichloroacetic acid  | µg/L                 | 0.7 | 4.4                           | 0.0      | 2.1           | 0.2      | 2.9           | 0.4      | 3.0           | 0.5      | 4.0           | 0.0      | 4.4           | 0.0      | 5.1                         | 0.1      | 3.6           | 0.0      | 3.6           | 0.0      |  |
| DBCAA   | Dibromochloroacetic acid  | µg/L                 | 1.0 | 3.2                           | 0.1      | 2.7           | 0.1      | 2.5           | 0.1      | 2.1           | 0.3      | 2.1           | 0.1      | 1.8           | 0.0      | 3.3                         | 0.2      | 2.5           | 0.0      | 2.0           | 0.0      |  |
| TBAA    | Tribromoacetic acid       | µg/L                 | 1.0 | 1.3                           | 0.1      | 2.3           | 0.5      | 3.4           | 0.3      | 4.6           | 0.1      | 4.3           | 0.1      | 2.5           | 0.0      | 1.6                         | 0.3      | 3.3           | 0.0      | 4.4           | 0.0      |  |
|         | Total HAAs                | µg/L                 |     | 28.4                          |          | 29.9          |          | 26.2          |          | 28.2          |          | 32.6          |          | 37.7          |          | 30.0                        |          | 29.4          |          | 34.4          |          |  |
| MCAN    | Monochloroacetonitrile    | µg/L                 | -   | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |  |
| MBAN    | Monobromoacetonitrile     | µg/L                 | 0.1 | 0.2                           | 0.0      | 0.3           | 0.1      | 0.3           | 0.0      | 0.5           | 0.0      | 0.5           | 0.0      | 0.3           | 0.0      | 0.3                         | 0.0      | 0.9           | 0.0      | 0.3           | 0.0      |  |
| DCAN    | Dichloroacetonitrile      | µg/L                 | 0.1 | 0.2                           | 0.0      | 0.4           | 0.1      | 0.3           | 0.0      | 0.2           | 0.0      | 1.0           | 0.1      | 1.1           | 0.1      | 0.5                         | 0.0      | 0.7           | 0.0      | 1.2           | 0.1      |  |
| TCAN    | Trichloroacetonitrile     | µg/L                 | 0.1 | 0.1                           | 0.0      | 0.3           | 0.1      | 0.2           | 0.0      | 0.3           | 0.0      | 0.7           | 0.0      | 0.8           | 0.1      | 0.4                         | 0.0      | 0.1           | 0.0      | 0.6           | 0.0      |  |
| DBAN    | Dibromoacetonitrile       | µg/L                 | 0.2 | 2.3                           | 0.1      | 1.6           | 0.0      | 0.8           | 0.0      | 0.5           | 0.1      | 2.6           | 0.0      | 2.8           | 0.0      | 1.0                         | 0.0      | 0.7           | 0.0      | 1.9           | 0.1      |  |
| BCAN    | Bromochloroacetonitrile   | µg/L                 | 0.2 | 0.2                           | 0.1      | 1.2           | 0.0      | 1.3           | 0.1      | 2.3           | 0.0      | 1.8           | 0.0      | 1.7           | 0.0      | 0.7                         | 0.0      | 1.8           | 0.0      | 1.6           | 0.0      |  |
| DBCAN   | Dibromochloroacetonitrile | µg/L                 | 0.5 | <0.5                          | -        | <0.5          | -        | <0.5          | -        | <0.5          | -        | <0.5          | -        | <0.5          | -        | <0.5                        | -        | <0.5          | -        | <0.5          | -        |  |
|         | Total HANs                | µg/L                 |     | 3.0                           |          | 3.7           |          | 3.0           |          | 3.8           |          | 6.6           |          | 6.6           |          | 2.9                         |          | 4.3           |          | 5.7           |          |  |
| MCAcAm  | Monochloroacetamide       | µg/L                 | -   | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |  |
| MBAcAm  | Monobromoacetamide        | µg/L                 | 0.1 | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        | <0.1          | -        | <0.1          | -        |  |
| DCAcAm  | Dichloroacetamide         | µg/L                 | 0.1 | 0.7                           | 0.0      | 0.7           | 0.0      | 1.0           | 0.0      | 0.8           | 0.0      | 0.7           | 0.0      | 1.0           | 0.0      | 1.1                         | 0.0      | 0.4           | 0.0      | 2.1           | 0.0      |  |
| TCAcAm  | Trichloroacetamide        | µg/L                 | 0.1 | <0.1                          | -        | <0.1          | -        | 0.1           | 0.0      | 0.1           | 0.0      | <0.1          | -        | <0.1          | -        | 0.1                         | 0.0      | 0.4           | 0.0      | 0.2           | 0.0      |  |
| DBAcAm  | Dibromoacetamide          | µg/L                 | 0.1 | 0.3                           | 0.0      | 0.1           | 0.0      | 0.8           | 0.0      | 0.4           | 0.0      | 0.3           | 0.0      | 0.1           | 0.0      | 0.1                         | 0.0      | 0.4           | 0.0      | 0.1           | 0.0      |  |
| BCAcAm  | Bromochloroacetamide      | µg/L                 | 0.1 | 0.5                           | 0.0      | 0.9           | 0.0      | 0.5           | 0.0      | 1.8           | 0.2      | 2.4           | 0.3      | 0.3           | 0.0      | 1.1                         | 0.0      | 1.7           | 0.0      | 0.5           | 0.0      |  |
| BDCAcAm | Bromodichloroacetamide    | µg/L                 | 0.1 | 0.2                           | 0.0      | 0.4           | 0.1      | 0.3           | 0.0      | 0.3           | 0.0      | 0.3           | 0.0      | 0.2           | 0.0      | 0.9                         | 0.0      | 0.5           | 0.0      | 0.3           | 0.0      |  |
| DBCACAm | Dibromochloroacetamide    | µg/L                 | 0.1 | 0.6                           | 0.2      | 0.8           | 0.2      | 1.0           | 0.1      | 1.1           | 0.1      | 0.2           | 0.0      | 0.3           | 0.1      | 0.5                         | 0.0      | 0.8           | 0.0      | 0.7           | 0.0      |  |
| TBAcAm  | Tribromoacetamide         | µg/L                 | 0.1 | 0.1                           | 0.0      | 0.2           | 0.0      | 0.3           | 0.0      | 0.3           | 0.0      | 1.2           | 0.1      | 0.6           | 0.0      | 0.2                         | 0.0      | 0.3           | 0.0      | 0.3           | 0.0      |  |
|         | Total HACams              | µg/L                 | 0.1 | 2.5                           |          | 3.1           |          | 4.1           |          | 4.7           |          | 5.0           |          | 2.6           |          | 3.9                         |          | 4.7           |          | 4.2           |          |  |
| NDMA    | N-nitrosodimethylamine    | ng/L                 | 0.1 | -                             |          | -             |          | -             |          | -             |          | -             |          | -             |          | <0.10                       |          | 0.9           |          | 0.8           |          |  |
|         | Quality parameters        |                      |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |  |
|         | TOC                       | mg/L C               |     | 4.1                           |          | 3.9           |          | 3.7           |          | 3.6           |          | 3.5           |          | 3.5           |          | 4.2                         |          | 4.1           |          | 4.0           |          |  |
|         | Temperature               | °C                   |     | 14.0                          |          | 14.0          |          | 14.0          |          | 14.0          |          | 14.0          |          | 14.0          |          | 14.2                        |          | 14.1          |          | 14.0          |          |  |
|         | Disinfectant residual     | mg/L Cl <sup>2</sup> |     | 0.6                           |          | 0.4           |          | 0.4           |          | 0.2           |          | 0.2           |          | 0.1           |          | 0.6                         |          | 0.5           |          | 0.4           |          |  |
|         | pH                        | µg/L                 |     | 7.0                           |          | 7.3           |          | 7.5           |          | 7.7           |          | 7.0           |          | 7.4           |          | 7.0                         |          | 7.4           |          | 7.5           |          |  |
|         | Bromate                   | µg/L                 |     |                               |          |               |          |               |          |               |          |               |          |               |          | 1.6                         |          |               |          |               |          |  |
|         | Bromide                   | µg/L                 |     | <12                           |          | <12           |          | <12           |          | <12           |          | <12           |          | <12           |          | <12                         |          | <12           |          | <12           |          |  |
|         | UV Abs                    |                      |     | 0.046                         |          | 0.042         |          | 0.045         |          | 0.043         |          | 0.042         |          | 0.042         |          | 0.066                       |          | 0.047         |          | 0.045         |          |  |
|         | SUVA                      |                      |     | 1.1                           |          | 1.1           |          | 1.2           |          | 1.2           |          | 1.2           |          | 1.2           |          | 1.6                         |          | 1.2           |          | 1.1           |          |  |

|                      |                              |       |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |
|----------------------|------------------------------|-------|-----|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|---------------|----------|---------------|----------|
| Date:                | 12/09/2016                   |       |     |                               |          |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |
| B                    |                              |       |     | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |               |          |               |          |
|                      |                              |       |     | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          | 6-12 h                      |          | 24-48 h       |          | 72-106 h      |          |
|                      | DBPs                         | Units | MDL | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. | Concentration | std dev. | Concentration | std dev. |
| CHCl <sub>3</sub>    | Chloroform                   | µg/L  | 0.4 | 4.5                           | 0.5      | 5.1           | 0.6      | 3.0           | 0.4      | 6.5           | 0.0      | 6.6           | 0.5      | 7.0           | 0.3      | 4.6                         | 0.0      | 4.0           | 0.1      | 4.6           | 0.5      |
| CHBrCl <sub>2</sub>  | Bromodichloromethane         | µg/L  | 0.3 | 6.6                           | 0.3      | 7.0           | 0.3      | 7.6           | 0.6      | 8.1           | 0.2      | 9.0           | 1.1      | 11.9          | 1.5      | 7.6                         | 0.1      | 8.1           | 0.1      | 9.1           | 1.3      |
| CHBr <sub>2</sub> Cl | Dibromochloromethane         | µg/L  | 0.2 | 35.7                          | 1.3      | 35.5          | 2.3      | 18.2          | 1.9      | 19.7          | 0.3      | 23.3          | 1.8      | 26.2          | 2.0      | 16.7                        | 0.0      | 19.3          | 0.3      | 26.1          | 1.6      |
| CHBr <sub>3</sub>    | Bromoform                    | µg/L  | 0.4 | 6.0                           | 0.4      | 10.5          | 0.2      | 13.1          | 0.4      | 20.3          | 0.2      | 20.6          | 1.2      | 26.5          | 1.6      | 8.2                         | 0.2      | 17.9          | 0.3      | 26.1          | 2.6      |
|                      | Total THMs                   |       |     | 52.8                          |          | 58.1          |          | 41.8          |          | 54.6          |          | 59.5          |          | 71.5          |          | 37.1                        |          | 49.3          |          | 65.9          |          |
| MCAA                 | Monochloroacetic acid        | µg/L  | 0.2 | 3.3                           | 0.4      | 4.0           | 0.4      | 4.8           | 0.6      | 4.1           | 0.5      | 3.5           | 0.6      | 4.0           | 0.4      | 4.4                         | 0.8      | 3.6           | 0.6      | 4.0           | 0.1      |
| MBAA                 | Monobromoacetic acid         | µg/L  | 0.5 | 0.6                           | 0.2      | 1.2           | 0.2      | 1.4           | 0.3      | 1.7           | 0.1      | 1.6           | 0.1      | 1.5           | 0.2      | 0.8                         | 0.1      | 0.8           | 0.1      | 1.0           | 0.0      |
| DCAA                 | Dichloroacetic acid          | µg/L  | 0.2 | 9.9                           | 1.2      | 10.9          | 1.2      | 12.8          | 0.5      | 15.4          | 0.9      | 13.8          | 0.0      | 13.1          | 1.2      | 11.2                        | 1.5      | 16.9          | 2.5      | 10.3          | 0.0      |
| TCAA                 | Trichloroacetic acid         | µg/L  | 0.2 | <0.2                          | -        | <0.2          | -        | 0.2           | 0.0      | 0.2           | 0.0      | 0.2           | 0.0      | 0.2           | -        | <0.2                        | -        | 0.2           | 0.0      | 0.5           | 0.0      |
| DBAA                 | Dibromoacetic acid           | µg/L  | 0.1 | 5.6                           | 0.8      | 6.2           | 0.8      | 7.4           | 0.1      | 8.9           | 0.4      | 8.0           | 0.5      | 7.6           | 0.8      | 5.7                         | 0.3      | 7.2           | 0.3      | 8.8           | 0.0      |
| BCAA                 | Bromochloroacetic acid       | µg/L  | 0.1 | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |
| BDCAA                | Bromodichloroacetic acid     | µg/L  | 0.7 | 4.4                           | 0.4      | 4.9           | 0.0      | 5.8           | 0.4      | 7.0           | 0.5      | 6.3           | 0.0      | 5.0           | 0.4      | 4.0                         | 0.9      | 4.4           | 0.3      | 3.6           | 0.0      |
| DBC AA               | Dibromochloroacetic acid     | µg/L  | 1.0 | 3.2                           | 0.1      | 3.6           | 0.1      | 4.3           | 0.1      | 5.1           | 0.3      | 4.6           | 0.0      | 4.2           | 0.1      | 2.1                         | 0.1      | 2.5           | 0.3      | 2.0           | 0.0      |
| TBAA                 | Tribromoacetic acid          | µg/L  | 1.0 | 1.3                           | 0.1      | 1.5           | 0.1      | 1.8           | 0.3      | 2.1           | 0.1      | 1.9           | 0.2      | 1.8           | 0.1      | 4.3                         | 0.1      | 2.5           | 0.5      | 4.4           | 0.0      |
|                      | Total HAAs                   |       |     | 28.3                          |          | 32.1          |          | 38.5          |          | 44.6          |          | 39.9          |          | 37.4          |          | 32.5                        |          | 38.2          |          | 34.6          |          |
| MCAN                 | Monochloroacetone nitrile    | µg/L  | -   | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        |
| MBAN                 | Monobromoacetone nitrile     | µg/L  | 0.1 | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        | <0.1          | -        | <0.1          | -        |
| DCAN                 | Dichloroacetone nitrile      | µg/L  | 0.1 | 0.5                           | 0.0      | 0.5           | 0.1      | 0.3           | 0.0      | 0.5           | 0.0      | 0.1           | 0.0      | 0.4           | 0.0      | 0.2                         | 0.0      | 0.2           | 0.1      | 0.3           | 0.0      |
| TCAN                 | Trichloroacetone nitrile     | µg/L  | 0.1 | 3.3                           | 0.3      | 3.1           | 0.2      | 2.1           | 0.3      | 4.7           | 0.9      | 1.3           | 0.1      | 2.1           | 0.1      | 1.9                         | 0.1      | 1.3           | 0.5      | 1.5           | 0.6      |
| DBAN                 | Dibromoacetone nitrile       | µg/L  | 0.2 | <0.1                          | -        | <0.1          | -        | 0.5           | 0.0      | <0.1          | -        | 1.2           | 0.0      | 1.2           | 0.5      | 0.5                         | 0.0      | 1.5           | 0.2      | 1.7           | 0.3      |
| BCAN                 | Bromochloroacetone nitrile   | µg/L  | 0.2 | <0.2                          | -        | <0.2          | -        | 0.5           | 0.0      | <0.2          | -        | 1.5           | 0.1      | 1.5           | 0.4      | 0.5                         | 0.0      | 1.5           | 0.1      | 1.2           | 0.3      |
| DBCAN                | Dibromochloroacetone nitrile | µg/L  | 0.5 | <0.5                          | -        |               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |

| Date:                | 19/10/2015               |       |                               |               |          |               |          |               |          |               |          |               |          |               |          |               |                             |               |          |               |          |               |          |  |  |  |  |  |  |  |
|----------------------|--------------------------|-------|-------------------------------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|-----------------------------|---------------|----------|---------------|----------|---------------|----------|--|--|--|--|--|--|--|
|                      | C                        |       | Simulation Distribution Tests |               |          |               |          |               |          |               |          |               |          |               |          |               | Actual Distribution Samples |               |          |               |          |               |          |  |  |  |  |  |  |  |
|                      |                          |       | 6 h                           |               | 12 h     |               | 24 h     |               | 48 h     |               | 72 h     |               | 106 h    |               | 6-12 h   |               | 12-24 h                     |               | 48-72 h  |               | 72-106 h |               |          |  |  |  |  |  |  |  |
|                      | DBPs                     | Units | MDL                           | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev.                    | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. |  |  |  |  |  |  |  |
| CHCl <sub>3</sub>    | Chloroform               | µg/L  | 0.4                           | 2.4           | 0.0      | 2.8           | 0.3      | 2.6           | 0.0      | 4.7           | 0.1      | 5.5           | 0.2      | 6.5           | 0.9      | 2.5           | 0.0                         | 2.6           | 0.0      | 7.5           | 0.2      | 7.9           | 0.3      |  |  |  |  |  |  |  |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L  | 0.3                           | 1.9           | 0.1      | 4.3           | 0.3      | 4.8           | 0.3      | 6.0           | 0.5      | 6.9           | 0.2      | 7.8           | 0.3      | 2.1           | 0.0                         | 4.6           | 0.0      | 5.0           | 0.2      | 8.5           | 0.2      |  |  |  |  |  |  |  |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L  | 0.2                           | 7.3           | 0.3      | 10.1          | 0.2      | 10.3          | 0.6      | 8.0           | 0.5      | 9.5           | 0.3      | 9.8           | 0.1      | 7.2           | 0.0                         | 10.9          | 0.0      | 10.3          | 0.3      | 10.2          | 0.2      |  |  |  |  |  |  |  |
| CHBr <sub>3</sub>    | Bromoform                | µg/L  | 0.4                           | 5.4           | 0.5      | 6.6           | 0.3      | 7.5           | 0.2      | 10.3          | 0.3      | 12.1          | 0.4      | 11.8          | 0.2      | 4.4           | 0.0                         | 6.8           | 0.0      | 8.8           | 0.2      | 10.5          | 0.3      |  |  |  |  |  |  |  |
|                      | Total THMs               | µg/L  |                               | 17.0          |          | 23.8          |          | 25.1          |          | 29.0          |          | 34.1          |          | 35.8          |          | 16.2          |                             | 24.9          |          | 31.6          |          | 37.1          |          |  |  |  |  |  |  |  |
| MCAA                 | Monochloroacetic acid    | µg/L  | 0.2                           | 3.4           | 0.0      | 3.6           | 0.1      | 4.6           | 0.0      | 3.6           | 0.0      | 3.6           | 0.0      | 3.7           | 0.0      | 3.5           | 0.0                         | 3.7           | 0.0      | 5.1           | 0.1      | 3.6           | 0.0      |  |  |  |  |  |  |  |
| MBAA                 | Monobromoacetic acid     | µg/L  | 0.5                           | 7.3           | 0.2      | 7.9           | 0.1      | 11.8          | 0.2      | nd            |          | nd            |          | nd            |          | 5.9           | 0.2                         | 6.3           | 0.2      | 6.5           | 0.1      | nd            |          |  |  |  |  |  |  |  |
| DCAA                 | Dichloroacetic acid      | µg/L  | 0.2                           | 2.0           | 0.3      | 2.3           | 0.1      | 4.0           | 0.0      | 4.0           | 0.3      | 4.4           | 0.3      | 4.0           | 0.1      | 2.1           | 0.0                         | 2.2           | 0.3      | 4.6           | 0.1      | 4             | 0.1      |  |  |  |  |  |  |  |
| TCAA                 | Trichloroacetic acid     | µg/L  | 0.2                           | 0.8           | 0.0      | 0.6           | 0.0      | 1.2           | 0.0      | <0.2          |          | <0.2          | 0.0      | <0.2          | 0.0      | 1.6           | 0.0                         | 1.8           | 0.0      | <0.2          |          | <0.2          |          |  |  |  |  |  |  |  |
| DBAA                 | Dibromoacetic acid       | µg/L  | 0.1                           | 12.7          | 0.1      | 17.8          | 0.2      | 18.4          | 0.3      | 13.2          | 0.0      | 13.0          | 0.0      | 13.0          | 0.0      | 13.0          | 0.3                         | 16.1          | 0.1      | nd            |          | nd            |          |  |  |  |  |  |  |  |
| BCAA                 | Bromochloroacetic acid   | µg/L  | 0.1                           | 2.8           | 0.1      | 3.8           | 0.2      | 4.5           | 0.3      | nd            |          | nd            |          | nd            |          | 2.2           | 0.3                         | 2.3           | 0.1      | nd            |          | nd            |          |  |  |  |  |  |  |  |
| BDCAA                | Bromodichloroacetic acid | µg/L  | 0.7                           | 9.0           | 0.1      | 6.7           | 0.1      | 8.0           | 0.4      | 7.0           | 0.0      | 6.9           | 0.0      | 6.8           | 0.0      | 8.3           | 0.4                         | 8.2           | 0.1      | 6.1           | 0.1      | nd            |          |  |  |  |  |  |  |  |
| DBCAA                | Dibromochloroacetic acid | µg/L  | 1                             | 5.3           | 0.0      | 4.6           | 0.1      | 5.0           | 0.6      | 5.4           | 0.1      | 5.4           | 0.2      | 5.3           | 0.2      | 5.3           | 0.6                         | 4.9           | 0.0      | <1            |          | <1            |          |  |  |  |  |  |  |  |
| TBAA                 | Tribromoacetic acid      | µg/L  | 1                             | 8.1           | 0.2      | 7.2           | 0.1      | 5.9           | 0.1      | 5.4           | 0.2      | 6             | 0.1      | 5.4           | 0.2      | 9.0           | 0.1                         | 8.2           | 0.2      | <1            |          | <1            |          |  |  |  |  |  |  |  |
|                      | Total HAAs               | µg/L  |                               | 51.4          |          | 54.5          |          | 63.4          |          | 38.6          |          | 39.2          |          | 38.2          |          | 50.9          |                             | 53.7          |          | 22.3          |          | 7.6           |          |  |  |  |  |  |  |  |
| MCAN                 | Monochloroacetonitrile   | µg/L  | -                             | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |                             | nd            |          | nd            |          | nd            |          |  |  |  |  |  |  |  |
| MBAN                 | Monobromoacetonitrile    | µg/L  | 0.1                           | <0.1          |          | <0.1          |          | <0.1          |          | <0.1          |          | <0.1          |          | <0.1          |          | <0.1          |                             | <0.1          |          | <0.1          |          | <0.1          |          |  |  |  |  |  |  |  |
| DCAN                 | Dichloroacetonitrile     | µg/L  | 0.1                           | 0.1           | 0.0      | 0.1           | 0.0      | 0.2           | 0.0      | 0.2           | 0.0      | 0.3           | 0.0      | 0.3           | 0.0      | <0.1          | 0.0                         | 0.2           | 0.0      | 0.3           | 0.0      | 0.2           | 0.0      |  |  |  |  |  |  |  |
| TCAN                 | Trichloroacetonitrile    | µg/L  | 0.1                           | <0.1          | 0.0      | 0.01          | 0.0      | <0.1          | 0.0      | <0.1          | 0.0      | <0.1          | 0.0      | <0.1          | 0.0      | <0.1          | 0.0                         | 0.01          | 0.0      | <0.1          | 0.0      | <0.1          | 0.0      |  |  |  |  |  |  |  |
| DBAN                 | Dibromoacetonitrile      | µg/L  | 0.2                           | 0.8           | 0.0      | 1.1           | 0.0      | 1.1           | 0.0      | 0.6           | 0.0      | 0.8           | 0.0      | 0.9           | 0.0      | <0.2          |                             |               |          |               |          |               |          |  |  |  |  |  |  |  |

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| Date:                | 19/10/2015               | D    |       |     | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |               |          |               |          |               |          |               |          |
|----------------------|--------------------------|------|-------|-----|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|
|                      |                          |      |       |     | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h                       |          | > 6 h         |          | 12-24 h       |          | 24-48 h       |          | 48-72         |          |
|                      |                          |      |       |     | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. |
|                      |                          | DBPs | Units | MDL |                               |          |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |               |          |               |          |
| CHCl <sub>3</sub>    | Chloroform               | µg/L | 0.4   |     | 9.5                           | 0.5      | 11.1          | 0.0      | 11.6          | 0.6      | 20.0          | 0.6      | 15.8          | 0.7      | 19.4                        | 0.4      | 10            | 0.3      | 11.6          | 0.0      | 15.9          | 0.5      | 17.8          | 0.0      |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L | 0.3   |     | 7.0                           | 0.1      | 7.7           | 0.2      | 8.0           | 0.3      | 11.0          | 0.4      | 8.4           | 0.6      | 10.8                        | 0.6      | 6.6           | 0.1      | 7.9           | 0.1      | 8.1           | 0.3      | 8.8           | 0.2      |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L | 0.2   |     | 2.9                           | 0.1      | 3.3           | 0.2      | 3.4           | 0.1      | 4.4           | 0.4      | 3.2           | 0.5      | 4.2                         | 0.4      | 2.8           | 0.0      | 3.3           | 0.0      | 3.5           | 0.1      | 4.0           | 0.2      |
| CHBr <sub>3</sub>    | Bromoform                | µg/L | 0.4   |     | <0.4                          | -        | 0.5           | 0.0      | 0.5           | 0.0      | 0.7           | 0.0      | 0.8           | 0.0      | 0.8                         | 0.0      | <0.7          | -        | <0.4          | -        | <0.4          | -        | 6.30          | 0.2      |
|                      | Total THMs               | µg/L |       |     | 19.3                          |          | 22.6          |          | 23.5          |          | 36.2          |          | 28.1          |          | 35.2                        |          | 19.4          |          | 22.8          |          | 27.5          |          | 36.9          |          |
| MCAA                 | Monochloroacetic acid    | µg/L | 0.2   |     | 3.5                           | 0.1      | 3.4           | 0.0      | 3.4           | 0.3      | 3.1           | 0.0      | 3.1           | 0.0      | 3.3                         | 0.0      | 3.8           | 0.3      | 3.7           | 0.0      | 3.1           | 0.0      | 3             | 0.0      |
| MBAA                 | Monobromoacetic acid     | µg/L | 0.5   |     | 5.8                           | 0.1      | 7.1           | 0.3      | 7.5           | 0.2      | nd            | -        | nd            | -        | nd                          | -        | 7.6           | 0.1      | 7.8           | 0.1      | nd            | -        | nd            | -        |
| DCAA                 | Dichloroacetic acid      | µg/L | 0.2   |     | 2.2                           | 0.1      | 2.5           | 0.0      | 2.7           | 0.0      | 4.0           | 0.2      | 4.7           | 0.2      | 4.9                         | 0.2      | 2.6           | 0.0      | 2.9           | 0.1      | 3.1           | 0.1      | 4.5           | 0.0      |
| TCAA                 | Trichloroacetic acid     | µg/L | 0.2   |     | 13.9                          | 0.5      | 15.0          | 0.5      | 15.3          | 0.0      | nd            | -        | nd            | -        | nd                          | -        | 13.0          | 0.4      | 15.5          | 0.3      | nd            | -        | nd            | -        |
| DBAA                 | Dibromoacetic acid       | µg/L | 0.2   |     | 1.6                           | 0.1      | 1.6           | 0.0      | 1.9           | 0.1      | <0.2          | -        | <0.2          | -        | <0.2                        | -        | 1.3           | 0.0      | 1.9           | 0.0      | <0.2          | -        | <0.2          | -        |
| BCAA                 | Bromochloroacetic acid   | µg/L | 0.1   |     | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |
| BDCAA                | Bromodichloroacetic acid | µg/L | 0.7   |     | 7.4                           | 0.2      | 7.8           | 0.3      | 7.9           | 0.1      | <0.7          | -        | <0.7          | -        | <0.7                        | -        | 7.6           | 0.2      | 7.9           | 0.2      | <0.7          | -        | <0.7          | -        |
| DBCAA                | Dibromochloroacetic acid | µg/L | 1     |     | 5.0                           | 0.0      | 5.1           | 0.0      | 5.2           | 0.0      | nd            | -        | nd            | -        | nd                          | -        | 4.6           | 0.1      | 5.3           | 0.1      | nd            | -        | nd            | -        |
| TBAA                 | Tribromoacetic acid      | µg/L | 1     |     | 8.1                           | 0.1      | 4.5           | 0.1      | 8.4           | 0.2      | 2.0           | 0.0      | 2.1           | 0.0      | 2.0                         | 0.0      | 8.5           | 0.0      | 6.5           | 0.0      | 2.0           | 0.0      | 2             | 0.0      |
|                      | Total HAAs               | µg/L |       |     | 47.4                          |          | 46.8          |          | 52.3          |          | 9.1           |          | 9.9           |          | 10.2                        |          | 49.0          |          | 51.5          |          | 8.2           |          | 9.5           |          |
| MCAN                 | Monochloroacetonitrile   | µg/L | -     |     | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd                          | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |
| MBAN                 | Monobromoacetonitrile    | µg/L | 0.1   |     | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        |
| DCAN                 | Dichloroacetonitrile     | µg/L | 0.1   |     | 0.9                           | 0.0      | 1.1           | 0.0      | 1.2           | 0.1      | 1.8           | 0.1      | 1.6           | 0.1      | 1.8                         | 0.1      | 0.5           | 0.0      | 1.0           | 0.0      | 1.3           | 0.1      | 1.5           | 0.0      |
| TCAN                 | Trichloroacetonitrile    | µg/L | 0.1   |     | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        | <0.1          | -        | <0.1          | 0.0      | <0.1          | 0.0      | 0.1           | 0.0      |
| DBAN                 | Dibromoacetonitrile      | µg/L | 0.2   |     | <0.2                          | -        |               |          |               |          |               |          |               |          |                             |          |               |          |               |          |               |          |               |          |

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| Date:   | 13/06/2016                |       |     |                               |          |               |          |               |          |               |          |               |          |               |          |               |          |               |          |                             |          |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---------|---------------------------|-------|-----|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|--|--|--|--|--|--|--|--|--|--|--|--|--|--|
| D       |                           |       |     | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|         |                           |       |     | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          | 6-12 h        |          | 24-48 h       |          | 48-72 h                     |          |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|         | DBPs                      | Units | MDL | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| CHCl3   | Chloroform                | µg/L  | 0.4 | 3.6                           | 0.4      | 5.3           | 0.2      | 6.0           | 0.1      | 6.7           | 0.1      | 7.8           | 0.0      | 8.5           | 0.4      | 4.2           | 0.1      | 7.2           | 0.1      | 8.9                         | 0.1      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| CHBrCl2 | Bromodichloromethane      | µg/L  | 0.3 | 5.0                           | 0.0      | 6.2           | 0.3      | 8.1           | 0.1      | 10.5          | 0.1      | 15.6          | 0.1      | 17.2          | 0.1      | 6.2           | 0.1      | 11.5          | 0.1      | 13.1                        | 4.8      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| CHBr2Cl | Dibromochloromethane      | µg/L  | 0.2 | 2.5                           | 0.0      | 4.4           | 0.4      | 5.5           | 0.0      | 6.9           | 0.1      | 7.5           | 0.3      | 8.8           | 0.3      | 3.7           | 0.2      | 7.2           | 0.1      | 8.0                         | 0.1      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| CHBr3   | Bromoform                 | µg/L  | 0.4 | 0.7                           | 0.1      | 0.4           | 0.0      | 0.4           | 0.0      | 0.5           | 0.0      | 0.6           | 0.1      | 0.7           | 0.1      | 0.6           | 0.1      | 0.8           | 0.0      | 0.9                         | 0.1      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|         | Total THMs                | µg/L  |     | 11.7                          |          | 16.2          |          | 20.0          |          | 24.5          |          | 31.4          |          | 35.2          |          | 14.6          |          | 26.6          |          | 30.8                        |          |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| MCAA    | Monochloroacetic acid     | µg/L  | 0.2 | 4.5                           | 0.2      | 4.2           | 0.2      | 4.0           | 0.1      | 4.2           | 0.3      | 3.8           | 0.2      | 3.6           | 0.3      | 4.1           | 0.1      | 3.9           | 0.3      | 4.0                         | 0.6      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| MBAA    | Monobromoacetic acid      | µg/L  | 0.5 | 2.3                           | 0.3      | 2.7           | 0.5      | 5.6           | 0.3      | 8.4           | 5.7      | 12.9          | 0.8      | 13.9          | 2.2      | 3.2           | 1.1      | 2.4           | 0.2      | 1.8                         | 0.3      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| DCAA    | Dichloroacetic acid       | µg/L  | 0.2 | 1.5                           | 0.0      | 1.8           | 0.2      | 1.9           | 0.2      | 5.9           | 0.3      | 4.9           | 0.7      | 7.0           | 0.4      | 2.0           | 0.3      | 1.0           | 0.6      | 1.8                         | 0.1      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| TCAA    | Trichloroacetic acid      | µg/L  | 0.2 | 0.4                           | 0.0      | 0.5           | 0.1      | 0.6           | 0.1      | 1.1           | 0.3      | 0.8           | 0.3      | 1.5           | 0.8      | 0.6           | 0.1      | 0.4           | 0.0      | 0.5                         | 0.2      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| DBAA    | Dibromoacetic acid        | µg/L  | 0.1 | 1.7                           | 0.0      | 2.0           | 0.3      | 2.5           | 0.5      | 5.6           | 1.7      | 4.9           | 2.6      | 6.4           | 0.2      | 2.2           | 0.0      | 1.0           | 0.1      | 1.1                         | 0.0      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| BCAA    | Bromochloroacetic acid    | µg/L  | 0.1 | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| BDCAA   | Bromodichloroacetic acid  | µg/L  | 0.7 | 2.4                           | 0.0      | 1.3           | 0.4      | 1.3           | 0.2      | 2.4           | 0.5      | 2.2           | 0.2      | 7.8           | 1.7      | 2.3           | 1.9      | 0.9           | 0.7      | 0.9                         | 0.0      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| DBCAA   | Dibromochloroacetic acid  | µg/L  | 1.0 | <1                            | -        | 2.1           | 0.1      | 1.0           | 0.1      | 2.1           | 1.0      | 1.8           | 1.0      | <1            |          | 1.1           | 0.0      | 1.5           | 1.3      | 1.0                         | 0.0      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| TBAA    | Tribromoacetic acid       | µg/L  | 1.0 | 6.0                           | 0.0      | 5.9           |          | 6.9           | 0.5      | 3.5           | 0.4      | 6.1           | 0.1      | 2.0           |          | 6.2           | 0.4      | 5.0           | 0.3      | 5.5                         | 0.5      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|         | Total HAAs                | µg/L  |     | 18.8                          |          | 20.6          |          | 23.7          |          | 33.2          |          | 37.4          |          | 42.2          |          | 21.5          |          | 16.2          |          | 16.6                        |          |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| MCAN    | Monochloroacetonitrile    | µg/L  | -   | nd                            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd                          |          |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| MBAN    | Monobromoacetonitrile     | µg/L  | 0.1 | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1                        | -        |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| DCAN    | Dichloroacetonitrile      | µg/L  | 0.1 | 0.5                           | 0.1      | 0.5           | 0.1      | 0.5           | 0.0      | 0.4           | 0.0      | 0.4           | 0.0      | 0.5           | 0.0      | 0.4           | 0.1      | 0.5           | 0.0      | 0.5                         | 0.0      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| TCAN    | Trichloroacetonitrile     | µg/L  | 0.1 | 0.8                           | 0.1      | 0.9           | 0.1      | 0.9           | 0.0      | 0.8           | 0.0      | 0.9           | 0.0      | 1.0           | 0.0      | 0.6           | 0.0      | 0.8           | 0.0      | 0.7                         | 0.0      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| DBAN    | Dibromoacetonitrile       | µg/L  | 0.2 | 0.2                           | 0.0      | 0.3           | 0.0      | 0.2           | 0.1      | 0.2           | 0.1      | 0.2           | 0.0      | 0.3           | 0.1      | 0.2           | 0.0      | 0.4           | 0.0      | 0.2                         | 0.0      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| BCAN    | Bromochloroacetonitrile   | µg/L  | 0.2 | 0.6                           | 0.1      | 1.2           | 0.0      | 0.4           | 0.1      | 0.2           | 0.1      | 0.2           | 0.1      | 0.2           | 0.1      | 0.4           | 0.0      | 0.4           | 0.1      | 0.3                         | 0.0      |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| DBCAN   | Dibromochloroacetonitrile | µg/L  | 0.5 | <0.5                          | -        | <0.5          | -        |               |          |               |          |               |          |               |          |               |          |               |          |                             |          |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

| Date:                | 18/10/2016               |       |      |  | Simulation Distribution Tests |          |               |          |               |          |               |          |               |          |               |          | Actual Distribution Samples |          |               |          |               |          |     |
|----------------------|--------------------------|-------|------|--|-------------------------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|-----------------------------|----------|---------------|----------|---------------|----------|-----|
|                      | D                        |       |      |  | 6 h                           |          | 12 h          |          | 24 h          |          | 48 h          |          | 72 h          |          | 106 h         |          | 6-12 h                      |          | 24-48 h       |          | 48-72 h       |          |     |
|                      | DBPs                     | Units | MDL  |  | Concentration                 | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration               | std dev. | Concentration | std dev. | Concentration | std dev. |     |
| CHCl <sub>3</sub>    | Chloroform               | µg/L  | 0.4  |  | 14.2                          | 0.5      | 15.5          | 0.0      | 16.9          | 0.6      | 17.7          | 0.6      | 18.6          | 0.7      | 19.6          | 0.4      |                             | 14.1     | 0.1           | 17.3     | 0.3           | 17.5     | 0.2 |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L  | 0.3  |  | 6.0                           | 0.1      | 7.1           | 0.2      | 7.9           | 0.3      | 8.3           | 0.4      | 8.7           | 0.6      | 9.1           | 0.6      |                             | 6.8      | 0.2           | 8.1      | 0.0           | 9.5      | 0.2 |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L  | 0.2  |  | 2.0                           | 0.1      | 2.6           | 0.2      | 3.1           | 0.1      | 3.7           | 0.4      | 5.1           | 0.5      | 6.0           | 0.4      |                             | 2.8      | 1.7           | 3.4      | 1.2           | 5.7      | 0.5 |
| CHBr <sub>3</sub>    | Bromoform                | µg/L  | 0.4  |  | 0.6                           | 0.0      | 0.6           | 0.0      | 0.6           | 0.0      | 0.8           | 0.0      | 1.0           | 0.1      | 1.2           | 0.1      |                             | 0.6      | 0.4           | 0.8      | 0.9           | 0.9      | 0.7 |
|                      | Total THMs               | µg/L  |      |  | 22.8                          |          | 25.8          |          | 28.5          |          | 30.6          |          | 33.4          |          | 35.9          |          |                             | 24.3     |               | 29.6     |               | 33.6     |     |
| MCAA                 | Monochloroacetic acid    | µg/L  | 0.2  |  | 3.5                           | 0.3      | 3.6           | 0.5      | 3.5           | 0.4      | 3.1           | 0.6      | 3.1           | 0.4      | 3.2           | 0.3      |                             | 3.4      | 1.9           | 3.9      | 0.4           | 3.5      | 0.1 |
| MBAA                 | Monobromoacetic acid     | µg/L  | 0.5  |  | 2.8                           | 0.0      | 3.0           | 0.6      | 3.1           | 0.4      | 2.2           | 0.1      | 2.5           | 0.6      | 3.0           | 0.6      |                             | 6.2      | 0.1           | 3.4      | 0.6           | 2.6      | 0.0 |
| DCAA                 | Dichloroacetic acid      | µg/L  | 0.2  |  | 2.0                           | 0.0      | 2.4           | 0.3      | 2.8           | 0.2      | 3.0           | 0.5      | 3.2           | 0.8      | 3.5           | 0.2      |                             | 2.5      | 0.7           | 3.1      | 0.8           | 3.3      | 0.1 |
| TCAA                 | Trichloroacetic acid     | µg/L  | 0.2  |  | 12.4                          | 0.2      | 12.6          | 0.2      | 13.6          | 4.3      | 9.5           | 2.1      | 11.0          | 0.2      | 13.0          | 2.1      |                             | 15.0     | 0.0           | 15.0     | 0.2           | 10.5     | 0.2 |
| DBAA                 | Dibromoacetic acid       | µg/L  | 0.2  |  | 2.0                           | 0.0      | 2.5           | 0.2      | 2.5           | 0.2      | 2.0           | 0.7      | 2.5           | 0.6      | 2.6           | 0.3      |                             | 1.6      | 2.0           | 2.8      | 0.6           | 2.6      | 0.0 |
| BCAA                 | Bromochloroacetic acid   | µg/L  | 0.2  |  | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | 0.1      | nd            | 0.1      |                             | nd       | -             | nd       | 0.1           | nd       | -   |
| BDCAA                | Bromodichloroacetic acid | µg/L  | 0.7  |  | 7.5                           | 0.4      | 7.9           | 0.8      | 8.0           | 2.6      | 4.1           | 0.4      | <0.7          | -        | <0.7          | -        |                             | 7.8      | 2.0           | 8.8      | 0.2           | 3.2      | 0.0 |
| DBCAA                | Dibromochloroacetic acid | µg/L  | 1    |  | 5.6                           | 1.4      | 5.8           | 0.1      | 5.8           | 0.4      | 6.2           | 1.5      | 7.0           | 0.9      | 8.30          | 0.5      |                             | 5.1      | 0.3           | 6.4      | 0.9           | 6.8      | 0.1 |
| TBAA                 | Tribromoacetic acid      | µg/L  | 1    |  | 9.0                           | 1.6      | 8.5           | 1.6      | 9.1           | 0.5      | 7.9           | 0.7      | 7.0           | 2.6      | 8.8           | 0.8      |                             | 4.5      | 0.9           | 10.0     | 2.6           | 8.3      | 0.8 |
|                      | Total HAAs               | µg/L  |      |  | 44.8                          |          | 46.3          |          | 48.4          |          | 38.0          |          | 36.3          |          | 42.4          |          |                             | 45.9     |               | 53.2     |               | 40.8     |     |
| MCAN                 | Monochloroacetonitrile   | µg/L  | -    |  | nd                            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        | nd            | -        |                             | nd       | -             | nd       | -             | nd       | -   |
| MBAN                 | Monobromoacetonitrile    | µg/L  | 0.1  |  | <0.1                          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        | <0.1          | -        |                             | <0.1     | -             | <0.1     | -             | <0.1     | -   |
| DCAN                 | Dichloroacetonitrile     | µg/L  | 0.1  |  | 1.0                           | 0.2      | 1.2           | 0.0      | 1.5           | 0.1      | 1.2           | 0.2      | 1.0           | 0.0      | 1.4           | 0.1      |                             | 1.7      | 0.3           | 2.0      | 0.0           | 1.5      | 0.3 |
| TCAN                 | Trichloroacetonitrile    | µg/L  | 0.2  |  | <0.2                          | -        | 0.5           | 0.1      | 0.9           | 0.1      | 1.5           | 0.2      | 1.0           | 0.2      | 1.8           | 0.0      |                             | <0.2     | 0.1           | <0.2     | 0.2           | 0.4      | 0.1 |
| DBAN                 | Dibromoacetonitrile      | µg/L  | 0.25 |  | 0.5                           | 0.2      | 0.7           | 0.1      | 0.3           | 0.1      | 0.3           | 0.1      | 0.3           | 0.1      | 0.2           | 0.0      |                             | 0.3      | 0.3           | 0.8      | 0.1           | 0.2      | 0.0 |
| BCAN                 | Bromochloroacetonitrile  | µg/L  | 0.25 |  | 0.6                           | 0.4      | 0.8           | 0.0      | 1.2           |          |               |          |               |          |               |          |                             |          |               |          |               |          |     |

## Appendix C. Database from the alternative disinfection experiments in the SDS tests

**Table C. 1:** Raw data of chlorination vs. chloramination in **WTW A** during **Round 2** (winter 16'-08/02/2016).

| Date: | 08/02/2016 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
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| Date:                | 09/05/2016               |               |                               |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |      |     |
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| A                    |                          |               |                               |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |      |     |
| DBPs                 | Units                    | MDL           | Simulation Distribution Tests |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |      |     |
|                      |                          |               | 6 h                           |               |                |               | 12 h         |               |                |               | 24 h         |               |                |               | 48 h         |               |                |               | 72 h         |               |                |               | 106 h        |               |                |      |     |
|                      |                          |               | Chlorination                  |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |      |     |
| Concentration        | std dev.                 | Concentration | std dev.                      | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       |      |     |
| CHCl <sub>3</sub>    | Chloroform               | µg/L          | 0.4                           | 4.3           | 0.1            | 2.5           | 0.5          | 7.0           | 0.5            | 0.9           | 0.2          | 8.3           | 0.2            | 1.7           | 0.2          | 9.3           | 0.2            | 2.1           | 0.1          | 10.6          | 0.3            | 4.6           | 0.5          | 11.8          | 0.0            | 5.1  | 0.1 |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L          | 0.3                           | 5.8           | 0.1            | 3.7           | 0.1          | 6.2           | 0.2            | 4.1           | 0.3          | 7.1           | 0.2            | 5.9           | 0.4          | 9.4           | 0.5            | 6.3           | 0.6          | 13.0          | 0.4            | 7.3           | 1.0          | 15.0          | 0.6            | 8.9  | 0.9 |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L          | 0.2                           | 13.5          | 0.3            | 10.0          | 0.2          | 14.6          | 0.0            | 12.1          | 0.3          | 18.6          | 0.7            | 15.0          | 0.4          | 19.3          | 2.1            | 15.2          | 0.5          | 19.5          | 0.1            | 16.0          | 0.5          | 20.3          | 0.4            | 16.6 | 1.0 |
| CHBr <sub>3</sub>    | Bromoform                | µg/L          | 0.4                           | 4.8           | 0.5            | 4.0           | 0.1          | 5.7           | 0.5            | 5.0           | 0.5          | 6.0           | 0.3            | 5.3           | 0.3          | 8.9           | 0.3            | 7.0           | 0.4          | 10.4          | 0.5            | 8.3           | 0.6          | 13.2          | 0.7            | 9.1  | 0.5 |
| Total THMs           |                          | µg/L          |                               | 28.3          |                | 20.2          |              | 33.6          |                | 22.1          |              | 40.0          |                | 27.9          |              | 46.9          |                | 30.6          |              | 53.5          |                | 36.2          |              | 60.3          |                | 39.7 |     |
| MCAA                 | Monochloroacetic acid    | µg/L          | 0.2                           | 4.0           | 0.2            | 2.4           | 0.1          | 3.5           | 0.5            | 1.9           | 0.0          | 3.8           | 0.1            | 2.6           | 0.1          | 3.0           | 0.1            | 2.6           | 0.5          | 2.4           | 0.2            | 3.2           | 0.1          | 3.5           | 0.3            | 3.6  | 0.0 |
| MBAA                 | Monobromoacetic acid     | µg/L          | 0.5                           | 1.0           | 0.2            | 0.8           | 0.2          | 1.1           | 0.6            | 0.5           | 0.0          | 1.2           | 0.5            | nd            | -            | 1.6           | 0.1            | <0.5          | -            | 0.4           | 0.0            | 0.8           | 0.1          | 1.1           | 0.1            | 0.4  | 0.0 |
| DCAA                 | Dichloroacetic acid      | µg/L          | 0.2                           | 11.2          | 0.1            | 0.6           | 0.1          | 13.4          | 0.2            | 0.8           | 0.0          | 17.3          | 0.0            | 3.6           | 0.0          | 10.5          | 0.1            | 0.8           | 0.1          | 6.6           | 0.1            | 0.8           | 0.1          | 10.6          | 0.1            | 0.5  | 0.0 |
| TCAA                 | Trichloroacetic acid     | µg/L          | 0.2                           | 1.0           | 0.1            | 0.9           | 0.0          | 0.7           | 0.1            | <0.2          | -            | 0.6           | 0.2            | 0.3           | 0.0          | 0.6           | 0.0            | <0.2          | -            | 0.7           | 0.1            | 0.6           | 0.0          | 0.6           | 0.0            | 0.5  | 0.0 |
| DBAA                 | Dibromoacetic acid       | µg/L          | 0.1                           | 5.9           | 0.3            | 1.3           | 0.1          | 8.9           | 0.2            | 1.5           | 0.0          | 8.7           | 0.1            | 3.6           | 0.3          | 8.8           | 0.4            | 2.1           | 0.2          | 10.5          | 0.2            | 1.8           | 0.3          | 8.5           | 0.0            | 1.1  | 0.0 |
| BCAA                 | Bromochloroacetic acid   | µg/L          | 0.1                           | 0.2           | 0.0            | <0.1          | -            | 0.1           | 0.0            | <0.1          | -            | nd            | -              | 0.4           | 0.0          | nd            | -              | <0.1          | -            | nd            | -              | <0.1          | -            | 0.1           | 0.0            | <0.1 | -   |
| BDCAA                | Bromodichloroacetic acid | µg/L          | 0.7                           | 4.7           | 0.1            | 1.4           | 0.0          | 5.0           | 0.0            | 1.8           | 0.0          | 5.2           | 0.5            | 3.1           | 0.0          | 5.4           | 0.1            | 1.2           | 0.2          | 3.9           | 0.0            | 1.5           | 0.4          | 6.3           | 0.2            | 4.3  | 0.1 |
| DBCAA                | Dibromochloroacetic acid | µg/L          | 1                             | 5.9           | 0.3            | 2.1           | 0.0          | 8.9           | 0.2            | 3.5           | 0.0          | 8.7           | 0.1            | 2.8           | 0.1          | 8.8           | 0.4            | 4.5           | 0.0          | 10.5          | 0.2            | 7.9           | 1.0          | 8.5           | 0.1            | 2.7  | 0.2 |
| TBAA                 | Trihalooacetic acid      | µg/L          | 1                             | 1.5           | 0.2            | 2.1           | 0.1          | 2.6           | 0.4            | 3.0           | 0.0          | 2.3           | 0.5            | 0.6           | 0.0          | 3.1           | 0.1            | 0.9           | 0.0          | 4.4           | 0.0            | 2.4           | 0.4          | 1.2           | 0.1            | 2.9  | 0.0 |
| Total HAAs           |                          | µg/L          |                               | 35.2          |                | 11.7          |              | 44.3          |                | 12.9          |              | 47.8          |                | 16.7          |              | 41.8          |                | 12.1          |              | 39.5          |                | 18.7          |              | 40.1          |                | 16.0 |     |
| MCAN                 | Monochloroacetanitrile   | µg/L          | -                             | nd            | -              | nd            | -            | nd            | -              | nd            | -            | nd            | -              | nd            | -            | nd            | -              | nd            | -            | nd            | -              | nd            | -            | nd            | -              | nd   | -   |
| MBAN                 | Monobromoacetanitrile    | µg/L          | 0.1                           | 0.6           | 0.2            |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |      |     |

| Date:                | 12/09/2016               |                               |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |          |     |
|----------------------|--------------------------|-------------------------------|---------------|----------------|---------------|--------------|---------------|----------------|---------------|--------------|---------------|----------------|---------------|--------------|---------------|----------------|---------------|--------------|---------------|----------------|---------------|--------------|---------------|----------------|---------------|----------|-----|
| A                    |                          |                               |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |          |     |
|                      |                          | Simulation Distribution Tests |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |          |     |
|                      |                          | 6 h                           |               |                |               | 12 h         |               |                |               | 24 h         |               |                |               | 48 h         |               |                |               | 72 h         |               |                |               | 106 h        |               |                |               |          |     |
|                      |                          | Chlorination                  |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |               | Chlorination |               | Chloramination |               |          |     |
| DBPs                 | Units                    | MDL                           | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev.     | Concentration | std dev.       | Concentration | std dev. |     |
| CHCl <sub>3</sub>    | Chloroform               | µg/L                          | 0.4           | 6.1            | 0.1           | 4.3          | 0.5           | 6.3            | 0.2           | 4.5          | 0.2           | 9.8            | 0.3           | 7.0          | 0.0           | 11.2           | 0.3           | 9.0          | 0.1           | 14.6           | 2.3           | 10.0         | 1.2           | 18.8           | 0.5           | 13.2     | 2.2 |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L                          | 0.3           | 8.7            | 0.1           | 6.2          | 0.2           | 9.8            | 0.2           | 6.5          | 0.5           | 11.3           | 0.4           | 7.9          | 0.6           | 14.4           | 0.3           | 11.5         | 0.7           | 18.2           | 3.5           | 14.6         | 2.1           | 21.4           | 0.2           | 15.0     | 1.5 |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L                          | 0.2           | 17.1           | 0.3           | 12.1         | 0.0           | 18.0           | 0.7           | 12.9         | 2.1           | 18.6           | 0.1           | 13.0         | 0.4           | 22.2           | 0.2           | 17.8         | 0.6           | 24.6           | 3.0           | 19.7         | 2.3           | 27.5           | 0.0           | 19.3     | 1.9 |
| CHBr <sub>3</sub>    | Bromoform                | µg/L                          | 0.4           | 5.5            | 0.5           | 3.9          | 0.5           | 6.1            | 0.3           | 4.0          | 0.3           | 5.9            | 0.5           | 4.1          | 0.7           | 7.0            | 0.5           | 5.6          | 0.6           | 7.2            | 0.5           | 5.8          | 1.3           | 7.7            | 0.5           | 5.4      | 0.3 |
| Total THMs           |                          | µg/L                          |               | 37.4           |               | 26.6         |               | 40.2           |               | 27.9         |               | 45.6           |               | 32.1         |               | 54.8           |               | 43.8         |               | 64.6           |               | 50.0         |               | 75.4           |               | 52.8     |     |
| MCAA                 | Monochloroacetic acid    | µg/L                          | 0.2           | 3.2            | 0.2           | 1.6          | 0.5           | 3.6            | 0.1           | 2.5          | 0.1           | 4.0            | 0.2           | 3.0          | 0.3           | 3.8            | 0.3           | 2.0          | 0.6           | 3.2            | 0.2           | 1.9          | 0.2           | 3.0            | 0.2           | 1.9      | 0.2 |
| MBAA                 | Monobromoacetic acid     | µg/L                          | 0.5           | 2.8            | 0.2           | 1.4          | 0.6           | 2.3            | 0.5           | 1.6          | 0.1           | 2.5            | 0.0           | 2.0          | 0.1           | 2.4            | 0.0           | 2.2          | 0.1           | 2.0            | 0.0           | 2.5          | 0.2           | 2.5            | 0.2           | 1.2      | 0.2 |
| DCAA                 | Dichloroacetic acid      | µg/L                          | 0.2           | 13.6           | 0.1           | 6.8          | 0.2           | 15.1           | 0.0           | 7.6          | 0.1           | 16.6           | 0.1           | 8.3          | 0.1           | 12.8           | 0.4           | 10.1         | 0.3           | 10.9           | 0.2           | 10.0         | 0.2           | 15.0           | 0.2           | 6.5      | 0.1 |
| TCAA                 | Trichloroacetic acid     | µg/L                          | 0.2           | 5.0            | 0.1           | 2.5          | 0.1           | 8.6            | 0.2           | 3.8          | 0.0           | 9.5            | 0.1           | 4.7          | 0.0           | 9.0            | 0.1           | 5.2          | 0.1           | 7.6            | 0.0           | 4.5          | 0.4           | 6.3            | 0.1           | 4.6      | 0.1 |
| DBAA                 | Dibromoacetic acid       | µg/L                          | 0.1           | 8.8            | 0.3           | 4.4          | 0.2           | 8.3            | 0.1           | 4.6          | 0.4           | 9.2            | 0.2           | 4.6          | 0.0           | 8.7            | 0.4           | 5.0          | 0.4           | 7.4            | 0.0           | 4.5          | 0.0           | 6.5            | 0.1           | 4.4      | 0.3 |
| BCAA                 | Bromochloroacetic acid   | µg/L                          | 0.1           | 9.9            | 0.0           | 5.0          | 0.0           | 10.4           | -             | 5.7          | 0.5           | 11.5           | -             | 5.7          | 0.0           | 10.9           | 0.0           | 6.3          | 0.0           | 9.3            | 1.2           | 5.0          | 0.2           | 6.0            | 1.0           | 5.6      | 0.0 |
| BDCAA                | Bromodichloroacetic acid | µg/L                          | 0.7           | 5.2            | 0.1           | 2.6          | 0.0           | 4.6            | 0.5           | 3.2          | 0.1           | 5.1            | 0.0           | 4.0          | 0.2           | 4.8            | 0.3           | 4.4          | 0.2           | 4.1            | 0.0           | 3.3          | 0.1           | 4.8            | 0.4           | 2.5      | 0.1 |
| TBAAA                | Dibromochloroacetic acid | µg/L                          | 1             | 6.6            | 0.3           | 3.3          | 0.2           | 6.5            | 0.1           | 3.6          | 0.4           | 7.2            | 0.2           | 4.6          | 0.1           | 6.5            | 0.3           | 5.1          | 0.8           | 5.5            | 0.0           | 2.5          | 0.1           | 8.0            | 0.0           | 3.3      | 0.3 |
| TBAA                 | Tri bromoacetic acid     | µg/L                          | 1             | 2.4            | 0.2           | 1.2          | 0.4           | 2.3            | 0.5           | 1.6          | 0.1           | 2.5            | 0.0           | 2.5          | 0.1           | 4.0            | 0.2           | 3.0          | 0.2           | 3.0            | 0.0           | 1.5          | 0.0           | 4.0            | 0.1           | 1.8      | 0.2 |
| Total HAAs           |                          | µg/L                          |               | 57.5           |               | 28.8         |               | 61.8           |               | 34.3         |               | 68.0           |               | 39.5         |               | 62.9           |               | 43.3         |               | 53.1           |               | 35.7         |               | 56.1           |               | 31.8     |     |
| MCAN                 | Monochloroacetoneitrile  | µg/L                          | -             | nd             | -             | nd           | -             | nd             | -             | nd           | -             | nd             | -             | nd           | -             | nd             | -             | nd           | -             | nd             | -             | nd           | -             | nd             | -             | nd       | -   |
| MBAN                 | Monobromoacetoneitrile   | µg/L                          | 0.1           | nd             | 0             |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |              |               |                |               |          |     |

| Date:                | 08/02/2016               |      |               |          | Simulation Distribution Tests |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |     |  |
|----------------------|--------------------------|------|---------------|----------|-------------------------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|-----|--|
| B                    |                          |      |               |          | 6 h                           |          |               |          | 12 h           |          |               |          | 24 h           |          |               |          | 48 h           |          |               |          | 72 h           |          |               |          | 106 h          |          |     |  |
| DBPs                 | Units                    | MDL  | Chlorination  |          | Chloramination                |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          |     |  |
|                      |                          |      | Concentration | std dev. | Concentration                 | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. |     |  |
| CHCl <sub>3</sub>    | Chloroform               | µg/L | 0.4           | 2.1      | 0.1                           | 1.9      | 0.0           | 2.6      | 0.1            | 2.1      | 0.0           | 2.7      | 0.1            | 2.2      | 0.1           | 2.8      | 0.0            | 2.3      | 0.0           | 3.3      | 0.1            | 2.4      | 0.0           | 3.5      | 0.1            | 2.6      | 0.0 |  |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L | 0.3           | 1.1      | 0.2                           | 0.8      | 0.0           | 2.3      | 0.0            | 1.1      | 0.0           | 4.4      | 0.2            | 2.5      | 0.1           | 3.8      | 0.2            | 3.4      | 0.1           | 6.1      | 0.1            | 5.1      | 0.0           | 7.1      | 0.0            | 5.6      | 0.0 |  |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L | 0.2           | 4.2      | 0.1                           | 3.4      | 0.0           | 5.1      | 0.3            | 5.4      | 0.0           | 8.4      | 0.4            | 6.6      | 0.0           | 9.8      | 0.3            | 7.6      | 0.0           | 10.7     | 0.3            | 8.0      | 0.0           | 12.2     | 0.5            | 10.1     | 0.1 |  |
| CHBr <sub>3</sub>    | Bromoform                | µg/L | 0.4           | 10.2     | 0.1                           | 6.8      | 0.1           | 11.3     | 0.1            | 7.2      | 0.1           | 15.7     | 0.0            | 11.0     | 0.1           | 17.0     | 0.2            | 11.8     | 0.2           | 18.0     | 0.3            | 12.3     | 0.2           | 20.1     | 0.5            | 13.6     | 0.3 |  |
| Total THMs           |                          | µg/L |               | 17.6     |                               | 12.9     |               | 21.3     |                | 15.8     |               | 31.3     |                | 22.3     |               | 33.3     |                | 25.1     |               | 38.2     |                | 27.8     |               | 42.9     |                | 31.9     |     |  |
| MCAA                 | Monochloroacetic acid    | µg/L | 0.2           | 3.3      | 0.1                           | 0.8      | 0.0           | 3.9      | 0.2            | 0.3      | 0.0           | 4.2      | 0.2            | 2.5      | 0.0           | 3.0      | 0.0            | 1.1      | 0.0           | 3.1      | 0.0            | 0.6      | 0.0           | 3.0      | 0.1            | 0.4      | 0.0 |  |
| MBAA                 | Monobromoacetic acid     | µg/L | 0.5           | 0.5      | 0.0                           | 0.6      | 0.0           | 0.5      | 0.0            | nd       | -             | 0.5      | 0.0            | 0.5      | 0.0           | 0.5      | 0.0            | nd       | -             | 0.7      | 0.0            | 0.5      | 0.0           | 0.7      | 0.0            | 0.6      | 0.0 |  |
| DCAA                 | Dichloroacetic acid      | µg/L | 0.2           | 1.1      | 0.1                           | 0.3      | 0.0           | 1.2      | 0.0            | 0.4      | 0.0           | 1.3      | 0.0            | 0.5      | 0.0           | 1.2      | 0.0            | <0.2     | -             | 1.0      | 0.0            | <0.2     | -             | 0.9      | 0.0            | <0.2     | -   |  |
| TCAA                 | Trichloroacetic acid     | µg/L | 0.2           | 0.9      | 0.0                           | 1.2      | 0.0           | 1.0      | 0.0            | 0.9      | 0.0           | 1.0      | 0.0            | 1.0      | 0.1           | 0.9      | 0.0            | 0.9      | 0.0           | 0.9      | 0.0            | 0.9      | 0.0           | 0.9      | 0.0            | 0.9      | 0.0 |  |
| DBAA                 | Dibromoacetic acid       | µg/L | 0.1           | 1.6      | 0.1                           | 1.4      | 0.0           | 1.7      | 0.0            | 1.0      | 0.0           | 1.7      | 0.0            | 1.3      | 0.0           | 1.7      | 0.0            | 1.0      | 0.0           | 1.9      | 0.0            | 1        | 0.0           | 2.0      | 0.0            | 1        | 0.0 |  |
| BCAA                 | Bromochloroacetic acid   | µg/L | 0.1           | nd       | -                             | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -   |  |
| BDCAA                | Bromodichloroacetic acid | µg/L | 0.7           | 1.2      | 0.0                           | 1.2      | 0.0           | 1.3      | 0.0            | 1.3      | 0.0           | 1.4      | 0.0            | 1.2      | 0.0           | 1.5      | 0.0            | 1.2      | 0.0           | 1.3      | 0.0            | 1.2      | 0.0           | 1.2      | 0.0            | 1.2      | 0.0 |  |
| DBCAA                | Dibromochloroacetic acid | µg/L | 1             | 1.1      | 0.1                           | <1       | -             | 1.4      | 0.0            | 1        | 0.0           | 1.0      | 0.0            | <1       | -             | 1.5      | 0.0            | 1.1      | 0.1           | 1.6      | 0.0            | 1.2      | 0.1           | 2.3      | 0.1            | 1        | 0.0 |  |
| TBAA                 | Tribromoacetic acid      | µg/L | 1             | 1.0      | 0.0                           | 1.8      | 0.1           | <1       | -              | 1.3      | 0.0           | 1.6      | 0.1            | <1       | -             | 1.1      | 0.0            | <1       | -             | 1.7      | 0.0            | <1       | -             | 1.6      | 0.1            | <1       | -   |  |
| Total HAAs           |                          | µg/L |               | 10.7     |                               | 7.2      |               | 10.9     |                | 6.2      |               | 12.7     |                | 7.0      |               | 11.4     |                | 5.3      |               | 12.2     |                | 5.5      |               | 12.6     |                | 5.1      |     |  |
| MCAN                 | Monochloroacetoneitrile  | µg/L | -             | nd       | -                             | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -             | nd       | -              | nd       | -   |  |
| MBAN                 | Monobromoacetoneitrile   | µg/L | 0.1           | <0.1     | -                             | 0.1      | 0.0           | <0.1     | -              | 0.1      | 0.0           | 0.1      | 0.0            | 0.1      | 0.0           | <0.1     | -              | <0.1     | -             | 0.1      |                |          |               |          |                |          |     |  |

| Date:                | 09/05/2016               |       |     | Simulation Distribution Tests |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |  |  |  |  |
|----------------------|--------------------------|-------|-----|-------------------------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|--|--|--|--|
|                      | DBPs                     | Units | MDL | 6 h                           |          |                |          |               |          | 12 h           |          |               |          | 24 h           |          |               |          | 48 h           |          |               |          | 72 h           |          |               |          | 106 h          |          |  |  |  |  |
|                      |                          |       |     | Chlorination                  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          |  |  |  |  |
|                      |                          |       |     | Concentration                 | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. |  |  |  |  |
| CHCl <sub>3</sub>    | Chloroform               | µg/L  | 0.4 | 4.4                           | 0.0      | 3.0            | 0.1      | 6.8           | 0.7      | 4.3            | 0.5      | 8.4           | 0.2      | 5.3            | 0.1      | 8.7           | 0.5      | 4.7            | 0.3      | 9.1           | 0.2      | 5.8            | 0.4      | 9.2           | 0.3      | 5.6            | 0.0      |  |  |  |  |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L  | 0.3 | 1.0                           | 0.1      |                |          | 2.8           | 0.0      |                |          | 4.4           | 0.0      |                |          | 5.1           | 0.0      |                |          | 6.5           | 0.3      |                |          | 8.4           | 0.0      |                |          |  |  |  |  |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L  | 0.2 | 6.5                           | 0.2      | 5.3            | 0.4      | 8.0           | 0.3      | 6.9            | 0.1      | 9.6           | 0.5      | 7.9            | 0.1      | 10.6          | 0.4      | 8.6            | 0.2      | 15.6          | 0.4      | 11.2           | 0.1      | 17.1          | 0.4      | 13.1           | 0.1      |  |  |  |  |
| CHBr <sub>3</sub>    | Bromoform                | µg/L  | 0.4 | 6.3                           | 0.1      | 2.9            | 0.6      | 6.5           | 0.1      | 4.5            | 0.4      | 7.6           | 0.2      | 6.1            | 0.3      | 8.4           | 0.3      | 7.7            | 0.1      | 11.7          | 0.0      | 8.1            | 0.8      | 16.4          | 0.8      | 14.7           | 0.6      |  |  |  |  |
|                      | <b>Total THMs</b>        | µg/L  |     | <b>18.3</b>                   |          | <b>11.2</b>    |          | <b>24.1</b>   |          | <b>15.6</b>    |          | <b>30.0</b>   |          | <b>19.2</b>    |          | <b>32.8</b>   |          | <b>21.0</b>    |          | <b>43.0</b>   |          | <b>25.1</b>    |          | <b>51.2</b>   |          | <b>33.5</b>    |          |  |  |  |  |
| MCAA                 | Monochloroacetic acid    | µg/L  | 0.2 | 3.3                           | 0.4      | 2.0            | 0.1      | 3.8           | 0.0      | 1.0            | 0.4      | 4.5           | 0.6      | 2.0            | 0.2      | 4.9           | 0.5      | 3.1            | 0.2      | 4.4           | 0.0      | 2.6            | 0.6      | 3.6           | 0.6      | 2.5            | 0.1      |  |  |  |  |
| MBAA                 | Monobromoacetic acid     | µg/L  | 0.5 | 0.6                           | 0.2      | 0.5            | 0.2      | 0.6           | 0.2      | <0.5           | -        | 0.6           | 0.3      | <0.5           | -        | 0.6           | 0.1      | <0.5           | -        | 0.8           | 0.1      | <0.5           | -        | 0.8           | 0.1      | 0.5            | 0.1      |  |  |  |  |
| DCAA                 | Dichloroacetic acid      | µg/L  | 0.2 | 9.9                           | 1.2      | 1.9            | 0.0      | 11.1          | 0.6      | 2.6            | 0.0      | 7.1           | 0.5      | 3.6            | 0.3      | 7.7           | 0.9      | 5.2            | 0.5      | 11.2          | 0.0      | 3.7            | 0.2      | 16.9          | 0.0      | 5.1            | 0.1      |  |  |  |  |
| TCAA                 | Trichloroacetic acid     | µg/L  | 0.2 | <0.2                          | -        | 0.5            | 0.1      | <0.2          | -        | <0.2           | -        | <0.2          | -        | 0.2            | 0.0      | 0.2           | 0.0      | 0.2            | 0.0      | 0.2           | 0.0      | 0.5            | 0.0      | 0.2           | 0.0      | <0.2           | -        |  |  |  |  |
| DBAA                 | Dibromoacetic acid       | µg/L  | 0.1 | 5.7                           | 0.8      | 1.9            | 0.0      | 7.3           | 0.0      | 2.6            | 0.2      | 5.1           | 0.1      | 3.1            | 0.6      | 5.0           | 0.4      | 4.1            | 0.0      | 5.7           | 0.1      | 3.5            | 0.3      | 7.2           | 0.0      | 3.7            | 0.1      |  |  |  |  |
| BCAA                 | Bromochloroacetic acid   | µg/L  | 0.1 | nd                            | -        | 0.1            | 0.0      | 0.1           | 0.0      | <0.1           | -        | 0.2           | 0.0      | <0.1           | -        | nd            | -        | <0.1           | -        | nd            | -        | 0.1            | 0.0      | 0.2           | 0.0      | <0.1           | -        |  |  |  |  |
| BDCAA                | Bromodichloroacetic acid | µg/L  | 0.7 | 4.4                           | 0.0      | 2.2            | 0.1      | 2.1           | 0.2      | 1.1            | 0.3      | 2.9           | 0.4      | 1.4            | 0.2      | 3.0           | 0.5      | 2.5            | 0.3      | 4.0           | 0.0      | 3.8            | 0.0      | 4.4           | 0.0      | 2.5            | 0.1      |  |  |  |  |
| DBCAA                | Dibromochloroacetic acid | µg/L  | 1   | 3.2                           | 0.1      | 2.9            | 0.1      | 2.7           | 0.1      | 2.1            | 0.2      | 2.5           | 0.1      | 1.4            | 0.3      | 2.1           | 0.3      | 2.6            | 0.3      | 2.1           | 0.1      | 2.2            | 0.1      | 1.8           | 0.0      | 2.1            | 0.0      |  |  |  |  |
| TBAA                 | Tribromoacetic acid      | µg/L  | 1   | 1.3                           | 0.1      | 1.0            | 0.2      | 2.3           | 0.5      | 1.5            | 0.3      | 3.4           | 0.3      | 1.8            | 0.3      | 4.6           | 0.1      | 1.8            | 0.1      | 4             | 0.1      | 2.1            | 0.4      | 2.5           | 0.0      | 1.7            | 0.3      |  |  |  |  |
|                      | <b>Total HAAs</b>        | µg/L  |     | <b>28.4</b>                   |          | <b>13.0</b>    |          | <b>29.9</b>   |          | <b>11.0</b>    |          | <b>26.2</b>   |          | <b>13.5</b>    |          | <b>28.2</b>   |          | <b>19.5</b>    |          | <b>32.6</b>   |          | <b>18.5</b>    |          | <b>37.7</b>   |          | <b>18.1</b>    |          |  |  |  |  |
| MCAN                 | Monochloroacetonitrile   | µg/L  | -   | nd                            | -        | nd             | -        | nd            | -        | nd             | -        | nd            | -        | nd             | -        | nd            | -        | nd             | -        | nd            | -        | nd             | -        | nd            | -        | nd             | -        |  |  |  |  |
| MBAN                 | Monobromoacetonitrile    | µg/L  | 0.1 | 0.2                           | 0.0      | 0.4            |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |  |  |  |  |

[illegible]

| Date:                | 14/03/2016               |      |     |                               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |
|----------------------|--------------------------|------|-----|-------------------------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|
|                      | C                        |      |     | Simulation Distribution Tests |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |
|                      |                          |      |     | 6 h                           |          |                |          | 12 h          |          |                |          | 24 h          |          |                |          | 48 h          |          |                |          | 72 h          |          |                |          | 106 h         |          |                |          |
|                      |                          |      |     | Chlorination                  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          |
|                      |                          |      |     | Concentration                 | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. |
| DBPs                 | Units                    | MDL  |     |                               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |
| CHCl <sub>3</sub>    | Chloroform               | µg/L | 0.4 | 1.5                           | 0.0      | 1.0            | 0.0      | 2.8           | 0.0      | 1.8            | 0.1      | 3.2           | 0.0      | 2.1            | 0.0      | 3.6           | 0.0      | 3.1            | 0.0      | 4.2           | 0.1      | 3.2            | 0.0      | 4.9           | 0.2      | 4.0            | 0.2      |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L | 0.3 | 4.0                           | 0.0      | 2.5            | 0.1      | 4.2           | 0.1      | 2.6            | 0.1      | 5.0           | 0.2      | 3.0            | 0.1      | 5.4           | 0.0      | 5.1            | 0.2      | 7.7           | 0.2      | 5.9            | 0.2      | 8.9           | 0.3      | 7.2            | 0.3      |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L | 0.2 | 8.3                           | 0.2      | 6.3            | 0.1      | 10.4          | 0.0      | 7.0            | 0.3      | 11.4          | 0.3      | 7.3            | 0.2      | 12.8          | 0.5      | 8.8            | 0.1      | 14.8          | 0.4      | 7.7            | 0.2      | 15.7          | 0.3      | 11.5           | 0.5      |
| CHBr <sub>3</sub>    | Bromoform                | µg/L | 0.4 | 10.6                          | 0.3      | 7.1            | 0.1      | 12.7          | 0.2      | 7.7            | 0.3      | 13.8          | 0.0      | 8.0            | 0.0      | 15.6          | 0.2      | 8.8            | 0.2      | 16.9          | 0.5      | 9.7            | 0.0      | 17.1          | 0.1      | 11.8           | 0.3      |
| Total THMs           |                          | µg/L |     | 24.5                          |          | 16.9           |          | 30.1          |          | 19.1           |          | 33.4          |          | 20.5           |          | 37.4          |          | 25.8           |          | 43.7          |          | 26.5           |          | 46.6          |          | 34.5           |          |
| MCAA                 | Monochloroacetic acid    | µg/L | 0.2 | 2.2                           | 0.1      | 1.8            | 0.2      | 2.7           | 0.0      | 2.0            | 0.2      | 2.0           | 0.0      | 2.4            | 0.1      | 0.5           | 0.0      | 4.3            | 0.1      | 1.7           | 0.1      | 3.5            | 0.3      | 2.9           | 0.1      | 2.3            | 0.1      |
| MBAA                 | Monobromoacetic acid     | µg/L | 0.5 | 1.4                           | 0.1      | 0.8            | 0.0      | 1.1           | 0.1      | 0.9            | 0.0      | 0.6           | 0.0      | 0.6            | 0.0      | nd            |          | 1.1            | 0.0      | 1.6           | 0.1      | 1.7            | 0.0      | 1.0           | 0.0      | 1.1            | 0.0      |
| DCAA                 | Dichloroacetic acid      | µg/L | 0.2 | 24.3                          | 0.6      | 22.9           | 0.1      | 18.6          | 0.7      | 14.4           | 0.1      | 16.1          | 0.3      | 13.5           | 0.2      | 16.7          | 0.4      | 15.7           | 0.6      | 16.0          | 0.5      | 16.5           | 0.6      | 12.3          | 0.4      | 13.7           | 0.1      |
| TCAA                 | Trichloroacetic acid     | µg/L | 0.2 | 0.3                           | 0.1      | 1.2            | 0.1      | 0.2           | 0.0      | 0.8            | 0.0      | 0.3           | 0.0      | 0.6            | 0.0      | <0.2          | -        | 0.9            | 0.0      | 0.8           | 0.1      | 1.2            | 0.0      | 0.3           | 0.0      | <0.2           | -        |
| DBAA                 | Dibromoacetic acid       | µg/L | 0.1 | 0.5                           | 0.0      | 0.1            | 0.0      | 1.1           | 0.0      | 0.4            | 0.0      | 0.5           | 0.0      | 1.2            | 0.1      | 0.4           | 0.0      | 0.2            | 0.1      | 0.5           | 0.0      | 0.3            | 0.0      | 0.4           | 0.1      | 0.1            | 0.0      |
| BCAA                 | Bromochloroacetic acid   | µg/L | 0.1 | nd                            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | 1.1            | 0.0      | 1.7           | 0.0      | 2.75           | 0.2      |
| BDCAA                | Bromodichloroacetic acid | µg/L | 0.7 | 0.6                           | 0.0      | 0.6            | 0.0      | 0.6           | 0.0      | 0.5            | 0.0      | 0.6           | 0.0      | 0.5            | 0.0      | 0.6           | 0.0      | 0.5            | 0.0      | 0.6           | 0.0      | 0.6            | 0.0      | 0.6           | 0.0      | 0.5            | 0.0      |
| DBCAA                | Dibromochloroacetic acid | µg/L | 1   | 2.3                           | 0.4      | 1.2            | 0.2      | 1.4           | 0.4      | 1.7            | 0.1      | 0.7           | 0.3      | 1.8            | 0.0      | 0.4           | 0.0      | 2.0            | 0.0      | 0.6           | 0.1      | 2.1            | 0.0      | 1.4           | 0.2      | 0.4            | 0.1      |
| TBAA                 | Tribromoacetic acid      | µg/L | 1   | 6.5                           | 0.2      | 4.9            | 0.1      | 3.9           | 0.1      | 2.2            | 0.0      | 2.1           | 0.0      | 1.7            | 0.0      | <1            | -        | <1             | -        | 1.0           | 0.1      | <1             | -        | <1            | -        | <1             | -        |
| Total HAAs           |                          | µg/L |     | 38.2                          |          | 33.5           |          | 29.6          |          | 22.9           |          | 22.9          |          | 22.4           |          | 18.6          |          | 24.8           |          | 22.7          |          | 26.9           |          | 20.7          |          | 20.8           |          |
| MCAN                 | Monochloroacetoneitrile  | µg/L | -   | nd                            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          |
| MBAN                 | Monobromoacetoneitrile   | µg/L | 0.1 | <0.1                          |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |

| Date:                | 13/06/2016               |       |     |                                      |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |  |  |  |  |
|----------------------|--------------------------|-------|-----|--------------------------------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|---------------|----------|----------------|----------|--|--|--|--|
|                      |                          |       |     | <b>C</b>                             |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |  |  |  |  |
|                      |                          |       |     | <b>Simulation Distribution Tests</b> |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |  |  |  |  |
|                      |                          |       |     | 6 h                                  |          |                |          | 12 h          |          |                |          | 24 h          |          |                |          | 48 h          |          |                |          | 72 h          |          |                |          | 106 h         |          |                |          |  |  |  |  |
|                      |                          |       |     | Chlorination                         |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          | Chlorination  |          | Chloramination |          |  |  |  |  |
|                      |                          |       |     | Concentration                        | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration  | std dev. |  |  |  |  |
|                      | DBPs                     | Units | MDL |                                      |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |  |  |  |  |
| CHCl <sub>3</sub>    | Chloroform               | µg/L  | 0.4 | 2.1                                  | 0.2      | 1.2            | 0.1      | 3.3           | 0.1      | 2.8            | 0.0      | 5.6           | 0.3      | 3.2            | 0.0      | 6.7           | 0.6      | 3.8            | 0.1      | 8.3           | 0.2      | 4.1            | 0.1      | 8.3           | 0.3      | 4.8            | 0.1      |  |  |  |  |
| CHBrCl <sub>2</sub>  | Bromodichloromethane     | µg/L  | 0.3 | 4.9                                  | 0.8      | 3.2            | 0.1      | 5.3           | 0.2      | 4.2            | 0.1      | 6.5           | 0.5      | 4.6            | 0.4      | 7.4           | 0.5      | 5.3            | 0.4      | 8.2           | 0.4      | 7.9            | 0.1      | 9.6           | 0.4      | 8.8            | 0.4      |  |  |  |  |
| CHBr <sub>2</sub> Cl | Dibromochloromethane     | µg/L  | 0.2 | 10.3                                 | 1.1      | 7.0            | 0.0      | 13.5          | 1.7      | 8.0            | 0.1      | 12.6          | 1.2      | 10.8           | 0.4      | 13.2          | 0.1      | 11.4           | 0.5      | 15.7          | 1.7      | 11.6           | 0.5      | 16.3          | 0.1      | 12.5           | 0.9      |  |  |  |  |
| CHBr <sub>3</sub>    | Bromoform                | µg/L  | 0.4 | 7.6                                  | 0.5      | 5.5            | 0.4      | 7.6           | 0.4      | 5.6            | 0.4      | 8.8           | 0.1      | 7.7            | 0.3      | 11.4          | 0.2      | 8.4            | 0.1      | 13.4          | 0.4      | 10.2           | 0.1      | 14.3          | 0.1      | 12.1           | 0.1      |  |  |  |  |
|                      | Total THMs               | µg/L  |     | 24.9                                 |          | 17.0           |          | 29.7          |          | 20.5           |          | 33.5          |          | 26.2           |          | 38.6          |          | 28.8           |          | 45.5          |          | 33.8           |          | 48.4          |          | 38.2           |          |  |  |  |  |
| MCAA                 | Monochloroacetic acid    | µg/L  | 0.2 | 1.9                                  | 0.5      | 2.2            | 1.0      | 4.9           | 1.9      | 2.6            | 0.8      | 3.2           | 0.2      | 2.7            | 0.1      | 3.9           | 0.4      | 3.5            | 0.5      | 4.6           | 1.0      | 4.2            | 0.0      | 4.4           | 0.6      | 3.5            | 0.3      |  |  |  |  |
| MBAA                 | Monobromoacetic acid     | µg/L  | 0.5 | 0.9                                  | 0.2      | <0.5           | -        | 3.6           | 0.1      | <0.5           | -        | 3.5           | 0.1      | <0.5           | -        | 4.5           | 0.3      | <0.5           | -        | 4.2           | 0.4      | <0.5           | -        | 5.0           | 0.9      | <0.5           | -        |  |  |  |  |
| DCAA                 | Dichloroacetic acid      | µg/L  | 0.2 | 5.7                                  | 1.8      | 4.3            | 0.7      | 14.5          | 0.7      | 5.1            | 0.4      | 13.6          | 1.7      | 4.7            | 0.4      | 17.9          | 0.5      | 5.4            | 0.7      | 19.2          | 0.8      | 6.3            | 0.0      | 20.4          | 1.2      | 5.7            | 0.5      |  |  |  |  |
| TCAA                 | Trichloroacetic acid     | µg/L  | 0.2 | 0.2                                  | 0.1      | 0.3            | 0.1      | <0.2          | -        | 0.6            | 0.0      | 0.2           | 0.0      | 0.4            | 0.1      | 0.3           | 0.0      | <0.2           | -        | 0.2           | 0.0      | 0.5            | 0.0      | 1.3           | 0.7      | 0.5            | 0.1      |  |  |  |  |
| DBAA                 | Dibromoacetic acid       | µg/L  | 0.1 | 2.5                                  | 0.5      | 1.0            | 0.2      | 6.2           | 2.0      | 1.2            | 0.1      | 7.5           | 1.2      | 1.1            | 0.2      | 9.6           | 0.8      | 1.1            | 0.1      | 9.0           | 0.4      | 1.9            | 0.1      | 12.5          | 1.4      | 1.3            | 0.1      |  |  |  |  |
| BCAA                 | Bromochloroacetic acid   | µg/L  | 0.1 | 2.1                                  | 0.3      | 0.6            | 0.0      | 0.4           | 0.0      | <0.1           | -        | 0.3           | 0.0      | <0.1           | -        | 0.5           | 0.0      | <0.1           | -        | 0.6           | 0.0      | <0.1           | -        | 0.5           | 0.1      | <0.1           | -        |  |  |  |  |
| BDCAA                | Bromodichloroacetic acid | µg/L  | 0.7 | 0.8                                  | 0.2      | 0.5            | 0.1      | 4.0           | 2.0      | 1.6            | 0.2      | 1.6           | 0.5      | 2.2            | 0.3      | 2.0           | 0.6      | 1.1            | 0.2      | 1.7           | 0.5      | 2.1            | 0.2      | 2.7           | 1.0      | 2.6            | 0.3      |  |  |  |  |
| DBCAA                | Dibromochloroacetic acid | µg/L  | 1   | <1                                   | -        | 2.0            | 0.0      | 5.5           | 0.3      | 4.0            | 0.0      | 7.5           | 0.8      | 5.0            | 0.0      | 5.5           | 0.3      | 7.5            | 0.0      | 5.8           | 0.7      | 1.4            | 0.0      | 6.2           | 0.3      | 2.5            | 0.0      |  |  |  |  |
| TBAA                 | Trihalooacetic acid      | µg/L  | 1   | 5.1                                  | 0.6      | 3.7            | 0.0      | 3.0           | 0.9      | 6.7            | 0.0      | 2.5           | 0.6      | 1.0            | 0.0      | 7.7           | 0.7      | 1.0            | 0.0      | 3.3           | 0.1      | 1.0            | 0.0      | 8.6           | 1.1      | 1.0            | 0.0      |  |  |  |  |
|                      | Total HAAs               | µg/L  |     | 19.1                                 |          | 14.6           |          | 42.1          |          | 21.8           |          | 39.9          |          | 17.2           |          | 51.8          |          | 19.6           |          | 48.6          |          | 17.3           |          | 61.5          |          | 17.1           |          |  |  |  |  |
| MCAN                 | Monochloroacetoneitrile  | µg/L  | -   | nd                                   |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          | nd            |          | nd             |          |  |  |  |  |
| MBAN                 | Monobromoacetoneitrile   | µg/L  | 0.1 | <                                    |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |               |          |                |          |  |  |  |  |

**Table C. 9:** Raw data of chlorination vs. chloramination in **WTW D** during **Round 3** (spring 16'-13/06/2016).

[illegible]

## Appendix D. Summary of Bromine Incorporation Factors

**Table D. 1:** Bromine incorporation factors of target DBPs in **WTW A** in various water ages during both chlorination and chloramination.

| DBPs          | 6 h       |                         | 12 h      |                         | 24 h      |                         | 48 h      |                         | 72 h      |                         | 106 h     |                         |
|---------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|
|               | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> |
| <b>THMs</b>   | 0.5       | 0.5                     | 0.5       | 0.5                     | 0.5       | 0.5                     | 0.5       | 0.5                     | 0.5       | 0.5                     | 0.4       | 0.4                     |
| <b>HAAs</b>   | 0.3       | 0.4                     | 0.3       | 0.4                     | 0.3       | 0.3                     | 0.4       | 0.4                     | 0.4       | 0.4                     | 0.4       | 0.4                     |
| Di-HAAs       | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.6                     |
| Tri-HAAs      | 0.5       | 0.6                     | 0.5       | 0.6                     | 0.5       | 0.4                     | 0.5       | 0.6                     | 0.6       | 0.5                     | 0.5       | 0.5                     |
| <b>HANs</b>   | 0.2       | 0.2                     | 0.3       | 0.2                     | 0.3       | -                       | 0.2       | -                       | 0.2       | 0.2                     | 0.2       | 0.2                     |
| <b>HAcAms</b> | 0.3       | 0.5                     | 0.3       | 0.4                     | 0.3       | 0.4                     | 0.3       | 0.4                     | 0.3       | 0.5                     | 0.2       | 0.3                     |
| Di-HAcAms     | 0.5       | 0.7                     | 0.5       | 0.7                     | 0.6       | 0.6                     | 0.5       | -                       | 0.5       | 0.7                     | 0.7       | 0.7                     |
| Tri-HAcAms    | 0.6       | 0.7                     | 0.4       | 0.6                     | 0.3       | 0.5                     | 0.3       | 0.6                     | 0.2       | 0.5                     | 0.1       | 0.3                     |

**Table D. 2:** Bromine incorporation factors of target DBPs in **WTW B** in various water ages during both chlorination and chloramination.

| DBPs          | 6 h       |                         | 12 h      |                         | 24 h      |                         | 48 h      |                         | 72 h      |                         | 106 h     |                         |
|---------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|
|               | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> |
| <b>THMs</b>   | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.7                     | 0.6       | 0.7                     | 0.7       | 0.7                     | 0.6       | 0.7                     |
| <b>HAAs</b>   | 0.3       | 0.4                     | 0.3       | 0.5                     | 0.4       | 0.3                     | 0.4       | 0.4                     | 0.3       | 0.4                     | 0.3       | 0.4                     |
| Di-HAAs       | 0.5       | 0.5                     | 0.5       | 0.6                     | 0.4       | 0.5                     | 0.5       | 0.6                     | 0.5       | 0.6                     | 0.5       | 0.5                     |
| Tri-HAAs      | 0.6       | 0.6                     | 0.5       | 0.6                     | 0.6       | 0.5                     | 0.6       | 0.5                     | 0.6       | 0.6                     | 0.6       | 0.6                     |
| <b>HANs</b>   | 0.4       | 0.0                     | 0.4       | 0.0                     | 0.4       | 0.2                     | 0.3       | 0.3                     | 0.2       | 0.4                     | 0.3       | 0.3                     |
| <b>HAcAms</b> | 0.3       | 0.4                     | 0.3       | 0.3                     | 0.4       | 0.4                     | 0.2       | 0.4                     | 0.3       | 0.2                     | 0.3       | 0.2                     |
| Di-HAcAms     | 0.6       | 0.8                     | 0.6       | 0.8                     | 0.5       | 0.8                     | 0.6       | 0.6                     | 0.5       | 0.7                     | 0.5       | 0.9                     |
| Tri-HAcAms    | 0.6       | 0.5                     | 0.6       | 0.3                     | 0.5       | 0.4                     | 0.1       | 0.6                     | 0.5       | 0.4                     | 0.2       | 0.2                     |

**Table D. 3:** Bromine incorporation factors of target DBPs in **WTW C** in various water ages during both chlorination and chloramination.

| DBPs          | 6 h       |                         | 12 h      |                         | 24 h      |                         | 48 h      |                         | 72 h      |                         | 106 h     |                         |
|---------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|
|               | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> |
| <b>THMs</b>   | 0.6       | 0.7                     | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.6                     |
| <b>HAAs</b>   | 0.3       | 0.3                     | 0.3       | 0.3                     | 0.3       | 0.3                     | 0.2       | 0.2                     | 0.2       | 0.2                     | 0.3       | 0.2                     |
| Di-HAAs       | 0.3       | 0.6                     | 0.3       | 0.6                     | 0.4       | 0.6                     | 0.4       | 0.5                     | 0.4       | 0.5                     | 0.3       | 0.3                     |
| Tri-HAAs      | 0.9       | 0.8                     | 0.7       | 0.7                     | 0.7       | 0.6                     | 0.6       | 0.6                     | 0.6       | 0.5                     | 0.6       | 0.5                     |
| <b>HANs</b>   | 0.4       | 0.3                     | 0.4       | 0.4                     | 0.4       | 0.2                     | 0.4       | 0.3                     | 0.4       | 0.1                     | 0.4       | 0.3                     |
| <b>HAcAms</b> | 0.4       | 0.4                     | 0.5       | 0.4                     | 0.4       | 0.4                     | 0.4       | 0.4                     | 0.4       | 0.4                     | 0.4       | 0.4                     |
| Di-HAcAms     | 0.4       | 0.3                     | 0.3       | 0.4                     | 0.3       | 0.4                     | 0.3       | 0.4                     | 0.2       | 0.3                     | 0.3       | 0.3                     |
| Tri-HAcAms    | 0.7       | 0.6                     | 0.7       | 0.7                     | 0.7       | 0.6                     | 0.5       | 0.4                     | 0.6       | 0.5                     | 0.5       | 0.4                     |

**Table D. 4:** Bromine incorporation factors of target DBPs in **WTW D** in various water ages during both chlorination and chloramination.

| DBPs          | 6 h       |                         | 12 h      |                         | 24 h      |                         | 48 h      |                         | 72 h      |                         | 106 h     |                         |
|---------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|-----------|-------------------------|
|               | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> | <i>Cl</i> | <i>NH<sub>2</sub>Cl</i> |
| <b>THMs</b>   | 0.3       | 0.3                     | 0.3       | 0.3                     | 0.3       | 0.3                     | 0.4       | 0.3                     | 0.4       | 0.3                     | 0.4       | 0.3                     |
| <b>HAAs</b>   | 0.4       | 0.5                     | 0.5       | 0.5                     | 0.5       | 0.5                     | 0.4       | 0.4                     | 0.5       | 0.4                     | 0.3       | 0.3                     |
| Di-HAAs       | 0.3       | 0.3                     | 0.3       | 0.3                     | 0.2       | 0.2                     | 0.2       | 0.3                     | 0.2       | 0.2                     | 0.2       | 0.2                     |
| Tri-HAAs      | 0.7       | 0.8                     | 0.7       | 0.8                     | 0.6       | 0.8                     | 0.6       | 0.6                     | 0.7       | 0.7                     | 0.5       | 0.4                     |
| <b>HANs</b>   | 0.3       | 0.2                     | 0.2       | 0.2                     | 0.2       | 0.1                     | 0.2       | 0.1                     | 0.1       | 0.1                     | 0.1       | 0.1                     |
| <b>HAcAms</b> | 0.4       | 0.3                     | 0.4       | 0.3                     | 0.3       | 0.3                     | 0.4       | 0.3                     | 0.3       | 0.4                     | 0.3       | 0.3                     |
| Di-HAcAms     | 0.4       | 0.3                     | 0.3       | 0.3                     | 0.3       | 0.4                     | 0.3       | 0.4                     | 0.3       | 0.4                     | 0.3       | 0.3                     |
| Tri-HAcAms    | 0.3       | 0.3                     | 0.5       | 0.3                     | 0.5       | 0.3                     | 0.5       | 0.1                     | 0.3       | 0.1                     | 0.5       | 0.2                     |

Appendix E. Database from the amide precursor experiments

Table E. 1: Raw data of chlorinated and chloraminated acetamide (screening and detailed phase).

| Acetamide            |                           | Chlorination  |          |               |          |               |          |               |          |               |          |               |          |               |          |               |          | Chloramination |          |               |          |               |          |               |          |               |          |               |          |               |          |               |          |
|----------------------|---------------------------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|----------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|---------------|----------|
|                      |                           | pH 7          |          |               |          |               |          |               |          | pH 8          |          |               |          |               |          |               |          | pH 7           |          |               |          |               |          |               |          | pH 8          |          |               |          |               |          |               |          |
|                      |                           | -             |          |               |          | with Br-      |          |               |          | -             |          |               |          | with Br-      |          |               |          | -              |          |               |          | with Br-      |          |               |          | -             |          |               |          | with Br-      |          |               |          |
|                      |                           | 4 h           |          | 24 h          |          | 4 h           |          | 24 h          |          | 4 h           |          | 24 h          |          | 4 h           |          | 24 h          |          | 4 h            |          | 24 h          |          | 4 h           |          | 24 h          |          | 4 h           |          | 24 h          |          | 4 h           |          | 24 h          |          |
|                      |                           | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration  | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. | Concentration | std dev. |
| DBPs                 | Units                     |               |          |               |          |               |          |               |          |               |          |               |          |               |          |               |          |                |          |               |          |               |          |               |          |               |          |               |          |               |          |               |          |
| CHCl <sub>3</sub>    | Chloroform                | nd            |          | nd            |          | nd            |          | nd            |          | 0.16          | 0.000    | 0.13          | 0.03     | bdl           |          | 0.048         | 0.000    | bdl            |          | bdl           |          | bdl           |          | bdl           |          | nd            |          | bdl           |          | bdl           |          | bdl           |          |
| CHBrCl <sub>2</sub>  | Bromodichloromethane      | -             |          | -             |          | nd            |          | nd            |          | -             |          | -             |          | bdl           |          | 0.032         | 0.00     | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | nd            |          | bdl           |          |
| CHBr <sub>2</sub> Cl | Dibromochloromethane      | -             |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | 0.013         | 0.000    | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          |
| CHBr <sub>3</sub>    | Bromoform                 | -             |          | -             |          | bdl           |          | bdl           | 0.0664   | -             |          | -             |          | bdl           |          | bdl           |          | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | nd            |          | bdl           |          |
| Total THMs           |                           | 0.0           |          | 0.0           |          | 0.0           |          | 0.1           |          | 0.16          |          | 0.13          |          | 0.0           |          | 0.09          |          | 0.0            |          | 0.0           |          | 0.0           |          | 0.0           |          | 0.0           |          | 0.0           |          | 0.0           |          | 0.0           |          |
| MCAA                 | Monochloroacetic acid     | 0.56          | 0.05     | 0.40          | 0.01     | 0.067         | 0.002    | 0.093         | 0.012    | 0.47          | 0.06     | bdl           |          | 0.56          | 0.02     | 0.400         | 0.012    | 0.19           | 0.03     | 0.15          | 0.09     | 0.43          | 0.03     | 0.74          | 0.25     | 0.63          | 0.11     | 0.11          | 0.028    | 0.46          | 0.03     | 0.45          | 0.04     |
| MBAA                 | Monobromoacetic acid      | -             |          | -             |          | nd            |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          |
| DCAA                 | Dichloroacetic acid       | bdl           |          | 0.061         | 0.006    | bdl           |          | 0.016         | 0.00     | 0.071         | 0.016    | 0.260         | 0.017    | 0.065         | 0.02     | bdl           |          | bdl            |          | bdl           |          | bdl           |          | 0.013         | 0.002    | bdl           |          | bdl           |          | 0.014         | 0.000    | bdl           |          |
| TCAA                 | Trichloroacetic acid      | bdl           |          | bdl           |          | bdl           |          | bdl           |          | 0.014         | 0.008    | 0.370         | 0.228    | bdl           |          | bdl           |          | bdl            |          | bdl           |          | bdl           |          | bdl           |          | 0.097         | 0.003    | bdl           |          | bdl           |          | bdl           |          |
| DBAA                 | Dibromoacetic acid        | -             |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          |
| BCAA                 | Bromochloroacetic acid    | -             |          | -             |          | bdl           |          | 0.039         | 0.014    | -             |          | -             |          | 0.069         | 0.005    | 0.052         | 0.006    | -              |          | -             |          | 0.049         | 0.01     | 0.029         | 0.008    | -             |          | -             |          | 0.033         | 0.002    | 0.039         | 0.018    |
| BDCAA                | Bromodichloroacetic acid  | -             |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          |
| DBCAA                | Dibromochloroacetic acid  | -             |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | 0.007         | 0.002    | bdl           |          | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          |
| TBAA                 | Trihaloacetic acid        | -             |          | -             |          | 0.015         | 0.000    | 0.015         | 0.001    | -             |          | -             |          | 0.021         | 0.001    | 0.011         | 0.002    | -              |          | -             |          | 0.007         | 0.002    | 0.007         | 0.003    | -             |          | -             |          | bdl           |          | bdl           |          |
| Total HAAs           |                           | 0.6           |          | 0.5           |          | 0.1           |          | 0.2           |          | 0.6           |          | 0.6           |          | 0.7           |          | 0.5           |          | 0.2            |          | 0.2           |          | 0.5           |          | 0.8           |          | 0.6           |          | 0.2           |          | 0.5           |          | 0.5           |          |
| MCAN                 | Monochloroacetanitrile    | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd             |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          |
| MBAN                 | Monobromoacetanitrile     | -             |          | -             |          | nd            |          | nd            |          | nd            |          | -             |          | nd            |          | nd            |          | -              |          | -             |          | nd            |          | nd            |          | -             |          | -             |          | nd            |          | nd            |          |
| DCAN                 | Dichloroacetanitrile      | nd            |          | nd            |          | nd            |          | nd            |          | bdl           |          | 0.025         | 0.011    | nd            |          | bdl           |          | bdl            |          | bdl           |          | bdl           |          | bdl           |          | bdl           |          | bdl           |          | bdl           |          | bdl           |          |
| TCAN                 | Trichloroacetanitrile     | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | 0.070         | 0.013    | nd            |          | nd            |          | bdl            |          | nd            |          | bdl           |          | bdl           |          | nd            |          | bdl           |          | nd            |          | nd            |          |
| DBAN                 | Dibromoacetanitrile       | -             |          | -             |          | nd            |          | nd            |          | -             |          | -             |          | nd            |          | nd            |          | -              |          | -             |          | nd            |          | nd            |          | -             |          | -             |          | nd            |          | nd            |          |
| BCAN                 | Bromochloroacetanitrile   | -             |          | -             |          | nd            |          | nd            |          | -             |          | -             |          | nd            |          | nd            |          | -              |          | -             |          | nd            |          | 0.047         |          | -             |          | -             |          | nd            |          | nd            |          |
| DBCAN                | Dibromochloroacetanitrile | -             |          | -             |          | nd            |          | nd            |          | -             |          | -             |          | nd            |          | nd            |          | -              |          | -             |          | nd            |          | nd            |          | -             |          | -             |          | nd            |          | nd            |          |
| Total HANs           |                           | 0.0           |          | 0.0           |          | 0.0           |          | 0.0           |          | 0.0           |          | 0.09          |          | 0.0           |          | 0.0           |          | 0.0            |          | 0.0           |          | 0.0           |          | 0.05          |          | 0.0           |          | 0.0           |          | 0.0           |          | 0.0           |          |
| MCACAn               | Monochloroacetamide       | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd             |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          | nd            |          |
| MBACAn               | Monobromoacetamide        | -             |          | -             |          | 0.020         |          | 0.113         | 0.00     | -             |          | -             |          | bdl           |          | 0.054         | 0.017    | -              |          | -             |          | bdl           |          | bdl           |          | -             |          | -             |          | bdl           |          | bdl           |          |
| DACACAn              | Dichloroacetamide         | 0.049         | 0.012    | bdl           |          | 0.045         | 0.007    | 0.241         | 0.007    | 0.042         | 0.008    | 0.076         | 0.022    | 0.037         | 0.001    | 0.023         | 0.012    | bdl            |          | bdl           |          | 0.045         | 0.020    | 0.038         | 0.003    | bdl           |          | 0.014         | 0.007    | bdl           |          | 0.011         | 0.001    |
| TACACAn              | Trichloroacetamide        | nd            |          | bdl           |          | 0.033         | 0.014    | 0.054         | 0.013    | 0.045         |          | 0.012         | 0.002    | 0.031         | 0.001    | 0.030         | 0.000    | bdl            |          | bdl           |          | 0.023         | 0.006    | 0.023         | 0.008    | bdl           |          | bdl           |          | 0.011         | 0.003    | 0.019         | 0.005    |
| DBACAn               | Dibromoacetamide          | -             |          | -             |          | 0.354         |          | 0.628         | 0.020    | -             |          | -             |          | 0.117         | 0.003    | 0.358         | 0.015    | -              |          | -             |          | 0.374         | 0.028    | 0.077         | 0.009    | -             |          | -             |          | 0.074         | 0.004    | 0.331         | 0.023    |
| BCACAn               | Bromochloroacetamide      | -             |          | -             |          | 0.427         |          | 0.371         | 0.011    | -             |          | -             |          | 0.145         | 0.004    | 0.039         | 0.000    | -              |          | -             |          | 0.043         | 0.018    | 0.050         | 0.001    | -             |          | -             |          | bdl           |          | 0.061         | 0.007    |
| BDCACAn              | Bromodichloroacetamide    | -             |          | -             |          | 0.196         | 0.034    | 0.065         | 0.03     | -             |          | -             |          | 0.141         | 0.031    | 0.032         | 0.010    | -              |          | -             |          | nd            |          | 0.008         | 0.002    | -             |          | -             |          | 0.060         | 0.006    | 0.036         | 0.001    |
| DBCACAn              | Dibromochloroacetamide    | -             |          | -             |          | 0.849         | 0.128    | 0.557         | 0.071    | -             |          | -             |          | 0.287         | 0.092    | 0.235         | 0.004    | -              |          | -             |          | 0.281         | 0.080    | 0.209         | 0.004    | -             |          | -             |          | 0.186         | 0.034    | 0.195         | 0.012    |
| TBACAn               | Trihaloacetamide          | -             |          | -             |          | 0.268         | 0.001    | 0.129         | 0.012    | -             |          | -             |          | 0.082         | 0.023    | 0.037         | 0.002    | -              |          | -             |          | 0.041         | 0.003    | 0.037         | 0.001    | -             |          | -             |          | 0.065         | 0.018    | 0.033         | 0.003    |
| Total HACams         |                           | 0.0           |          | 0.000         |          | 2.191         |          | 2.158         |          | 0.088         |          | 0.088         |          | 0.840         |          | 0.808         |          | 0.000          |          | 0.000         |          | 0.807         |          | 0.442         |          | 0.900         |          | 0.014         |          | 0.397         |          | 0.687         |          |

**Table E. 2:** Raw data of chlorinated and chloraminated **acetoacetamide** (screening and detailed phase).

| Acetoacetamide       |                           | Chlorination  |         |               |         |               |         |               |         |               |         |               |         |               |         |               |         | Chloramination |         |               |         |               |         |               |         |               |         |               |         |               |         |       |      |
|----------------------|---------------------------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|----------------|---------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|---------------|---------|-------|------|
|                      |                           | pH 7          |         |               |         |               |         |               |         | pH 8          |         |               |         |               |         |               |         | pH 7           |         |               |         |               |         |               |         | pH 8          |         |               |         |               |         |       |      |
|                      |                           | -             |         |               |         | with Br-      |         |               |         | -             |         |               |         | with Br-      |         |               |         | -              |         |               |         | with Br-      |         |               |         | -             |         |               |         | with Br-      |         |       |      |
|                      |                           | 4 h           |         | 24 h          |         | 4 h           |         | 24 h          |         | 4 h           |         | 24 h          |         | 4 h           |         | 24 h          |         | 4 h            |         | 24 h          |         | 4 h           |         | 24 h          |         | 4 h           |         | 24 h          |         | 4 h           |         | 24 h  |      |
|                      |                           | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration  | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev | Concentration | std dev |       |      |
| DBPs                 |                           | Units         |         |               |         |               |         |               |         |               |         |               |         |               |         |               |         |                |         |               |         |               |         |               |         |               |         |               |         |               |         |       |      |
| CHCl <sub>3</sub>    | Chloroform                | bdl           |         | bdl           |         | bdl           |         | bdl           |         | 0.1589        | 0.0010  | 0.1573        | 0.00    | 0.06          | 0.00    | 0.19          | 0.00    | 0.016          |         | 0.04          |         | bdl           |         | 0.01          |         | bdl           |         | bdl           |         | 0.012         |         | 0.03  |      |
| CHBrCl <sub>2</sub>  | Bromodichloromethane      | -             |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | bdl           |         | 0.10          | 0.04    | -              |         | -             |         | 0.02          |         | bdl           |         | -             |         | -             |         | bdl           |         | bdl   |      |
| CHBr <sub>2</sub> Cl | Dibromochloromethane      | -             |         | -             |         | bdl           |         | 0.30          | 0.00    | -             |         | -             |         | 0.01          | 0.00    | bdl           |         | -              |         | -             |         | bdl           |         | 0.01          |         | -             |         | -             |         | bdl           |         | bdl   |      |
| CHBr <sub>3</sub>    | Bromoform                 | -             |         | -             |         | bdl           |         | 0.17          | 0.02    | -             |         | -             |         | 0.30          | 0.01    | 0.31          | 0.00    | -              |         | -             |         | 0.01          |         | 0.01          |         | -             |         | -             |         | bdl           |         | bdl   |      |
| Total THMs           |                           | 0.0           |         | 0.0           |         | 0.0           |         | 0.5           |         | 0.2           |         | 0.2           |         | 0.371         |         | 0.598         |         | 0.016          |         | 0.040         |         | 0.022         |         | 0.027         |         | 0.000         |         | 0.000         |         | 0.012         |         | 0.032 |      |
| MCAA                 | Monochloroacetic acid     | 0.47          | 0.12    | 0.48          | 0.05    | 0.56          | 0.10    | 0.44          | 0.04    | 0.21          | 0.02    | 0.291         | 0.003   | 0.64          | 0.31    | 0.51          | 0.23    | 0.14           | 0.02    | 0.05          | 0.01    | 0.09          | 0.02    | 0.05          | 0.00    | 0.39          | 0.02    | 0.05          | 0.01    | 0.35          | 0.00    | 0.15  | 0.00 |
| MBAA                 | Monobromoacetic acid      | -             |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | bdl           |         | bdl           |         | -              |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | bdl           |         | bdl   |      |
| DCAA                 | Dichloroacetic acid       | 0.07          | 0.00    | 0.07          | 0.00    | 0.07          | 0.01    | 0.060         | 0.00    | 0.33          | 0.00    | 0.304         | 0.005   | 0.06          | 0.00    | 0.09          | 0.00    | bdl            |         | bdl           |         | bdl           |         | bdl           |         | bdl           |         | bdl           |         | bdl           |         | bdl   |      |
| TCAA                 | Trichloroacetic acid      | bdl           |         | bdl           |         | bdl           |         | bdl           |         | 0.01          | 0.00    | bdl           |         | bdl           |         | bdl           |         | bdl            |         | bdl           |         | bdl           |         | bdl           |         | bdl           |         | 0.10          | 0.03    | bdl           |         | bdl   |      |
| DBAA                 | Dibromoacetic acid        | -             |         | -             |         | 0.04          | 0.00    | 0.051         | 0.00    | -             |         | -             |         | 0.05          | 0.00    | 0.05          | 0.01    | -              |         | -             |         | 0.05          | 0.00    | 0.04          | 0.00    | -             |         | -             |         | 0.04          | 0.01    | 0.03  | 0.00 |
| BCAA                 | Bromochloroacetic acid    | -             |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | bdl           |         | bdl           |         | -              |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | bdl           |         | bdl   |      |
| BDCAA                | Bromodichloroacetic acid  | -             |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | bdl           |         | bdl           |         | -              |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | bdl           |         | bdl   |      |
| DBCAA                | Dibromochloroacetic acid  | -             |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | 0.01          | 0.00    | 0.01          | 0.00    | -              |         | -             |         | 0.01          | 0.00    | bdl           |         | -             |         | -             |         | bdl           |         | 0.01  | 0.00 |
| TBAA                 | Trihaloacetic acid        | -             |         | -             |         | 0.012         | 0.001   | 0.014         | 0.00    | -             |         | -             |         | 0.01          | 0.00    | bdl           |         | -              |         | -             |         | bdl           |         | 0.01          | 0.00    | -             |         | -             |         | 0.02          | 0.00    | 0.01  | 0.00 |
| Total HAAs           |                           | 0.5           |         | 0.5           |         | 0.7           |         | 0.6           |         | 0.6           |         | 0.6           |         | 0.8           |         | 0.7           |         | 0.14           |         | 0.05          |         | 0.15          |         | 0.10          |         | 0.39          |         | 0.2           |         | 0.4           |         | 0.2   |      |
| MCAN                 | Monochloroacetanitrile    | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd             |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd    |      |
| MBAN                 | Monobromoacetanitrile     | -             |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd            |         | -              |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd    |      |
| DCAN                 | Dichloroacetanitrile      | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | 0.026         | 0.003   | nd            |         | nd            |         | nd             |         | nd            |         | nd            |         | nd            |         | nd            |         | bdl           |         | nd            |         | nd    |      |
| TCAN                 | Trichloroacetanitrile     | nd            |         | nd            |         | nd            |         | nd            |         | -             |         | 0.063         | 0.000   | nd            |         | nd            |         | nd             |         | nd            |         | nd            |         | nd            |         | nd            |         | 0.02          | 0.01    | nd            |         | nd    |      |
| DBAN                 | Dibromoacetanitrile       | -             |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd            |         | -              |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd    |      |
| BCAN                 | Bromochloroacetanitrile   | -             |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd            |         | -              |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd    |      |
| DBCAN                | Dibromochloroacetanitrile | -             |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd            |         | -              |         | -             |         | nd            |         | nd            |         | -             |         | -             |         | nd            |         | nd    |      |
| Total HANs           |                           | 0.0           |         | 0.0           |         | 0.0           |         | 0.0           |         | 0.0           |         | 0.1           |         | 0.0           |         | 0.0           |         | 0.0            |         | 0.0           |         | 0.0           |         | 0.0           |         | 0.0           |         | 0.0           |         | 0.0           |         | 0.0   |      |
| MCaAcAr              | Monochloroacetamide       | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd             |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd            |         | nd    |      |
| MBaAcAr              | Monobromoacetamide        | -             |         | -             |         | bdl           |         | bdl           |         | -             |         | -             |         | 0.01          | 0.01    | 0.04          | 0.01    | -              |         | -             |         | 0.01          | 0.00    | bdl           |         | -             |         | -             |         | bdl           |         | 0.05  | 0.00 |
| DCAcAr               | Dichloroacetamide         | bdl           |         | 0.24          | 0.05    | bdl           |         | 0.03          | 0.01    | 0.094         | 0.015   | 0.144         | 0.003   | 0.03          | 0.00    | 0.04          | 0.02    | 0.04           | 0.00    | 0.01          | 0.00    | 0.03          | 0.01    | 0.03          | 0.00    | bdl           |         | 0.04          | 0.01    | bdl           |         | 0.04  | 0.00 |
| TCaAcAr              | Trichloroacetamide        | 0.12          | 0.00    | 0.02          | 0.01    | bdl           |         | 0.03          | 0.00    | 0.037         | 0.005   | 0.076         | 0.005   | 0.10          | 0.11    | 0.03          | 0.00    | bdl            |         | bdl           |         | 0.01          | 0.00    | 0.03          | 0.01    | bdl           |         | 0.40          | 0.00    | bdl           |         | 0.01  | 0.00 |
| DBaAcAr              | Dibromoacetamide          | -             |         | -             |         | 0.42          | 0.02    | 0.11          | 0.04    | -             |         | -             |         | 0.11          | 0.02    | 0.30          | 0.00    | -              |         | -             |         | 0.34          | 0.03    | 0.05          | 0.00    | -             |         | -             |         | 0.05          | 0.01    | 0.29  | 0.02 |
| BCaAcAr              | Bromochloroacetamide      | -             |         | -             |         | 0.21          | 0.00    | 0.32          | 0.01    | -             |         | -             |         | bdl           |         | 0.04          | 0.01    | -              |         | -             |         | 0.08          | 0.01    | 0.05          | 0.01    | -             |         | -             |         | 0.08          | 0.03    | 0.03  | 0.00 |
| BDCaAcAr             | Bromodichloroacetamide    | -             |         | -             |         | 0.08          | 0.01    | 0.04          | 0.00    | -             |         | -             |         | bdl           |         | 0.03          | 0.01    | -              |         | -             |         | 0.02          | 0.00    | 0.03          | 0.00    | -             |         | -             |         | 0.04          | 0.00    | 0.03  | 0.00 |
| DBCACaAr             | Dibromochloroacetamide    | -             |         | -             |         | 0.44          | 0.00    | 0.55          | 0.00    | -             |         | -             |         | 0.18          | 0.04    | 0.20          | 0.00    | -              |         | -             |         | 0.23          | 0.02    | 0.22          | 0.04    | -             |         | -             |         | 0.25          | 0.02    | 0.19  | 0.00 |
| TBaAcAr              | Trihaloacetamide          | -             |         | -             |         | 0.10          | 0.00    | 0.12          | 0.02    | -             |         | -             |         | 0.07          | 0.03    | 0.03          | 0.00    | -              |         | -             |         | 0.03          | 0.00    | 0.04          | 0.01    | -             |         | -             |         | 0.04          | 0.00    | 0.04  | 0.00 |
| Total HAaAms         |                           | 0.12          |         | 0.3           |         | 1.3           |         | 1.2           |         | 0.13          |         | 0.2           |         | 0.5           |         | 0.7           |         | 0.0            |         | 0.0           |         | 0.7           |         | 0.4           |         | 0.0           |         | 0.4           |         | 0.5           |         | 0.7   |      |

**Table E. 3:** Raw data of chlorinated and chloraminated **polyacrylamide** (screening and detailed phase).

| Polyacrylamide            |       | Units    |       | Chlorination  |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       | Chloramination |       |          |       |               |       |          |       |               |       |          |       |          |  |  |  |
|---------------------------|-------|----------|-------|---------------|-------|----------|-------|---------------|-------|----------|-------|---------------|-------|----------|-------|---------------|-------|----------|-------|----------------|-------|----------|-------|---------------|-------|----------|-------|---------------|-------|----------|-------|----------|--|--|--|
|                           |       |          |       | pH7           |       |          |       |               |       |          |       | pH8           |       |          |       |               |       |          |       | pH7            |       |          |       |               |       |          |       | pH8           |       |          |       |          |  |  |  |
|                           |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |                |       |          |       |               |       |          |       |               |       |          |       |          |  |  |  |
|                           |       |          |       | -             |       |          |       | with Br-      |       |          |       | -             |       |          |       | with Br-      |       |          |       | -              |       |          |       | with Br-      |       |          |       | -             |       |          |       | with Br- |  |  |  |
|                           |       |          |       | 4 h           | 24 h  | 4 h      | 24 h  | 4 h           | 24 h  | 4 h      | 24 h  | 4 h           | 24 h  | 4 h      | 24 h  | 4 h           | 24 h  | 4 h      | 24 h  | 4 h            | 24 h  | 4 h      | 24 h  | 4 h           | 24 h  | 4 h      | 24 h  | 4 h           | 24 h  | 4 h      | 24 h  |          |  |  |  |
| Concentration             |       | std dev. |       | Concentration |       | std dev. |       | Concentration |       | std dev. |       | Concentration |       | std dev. |       | Concentration |       | std dev. |       | Concentration  |       | std dev. |       | Concentration |       | std dev. |       | Concentration |       | std dev. |       |          |  |  |  |
| DBPs                      |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |                |       |          |       |               |       |          |       |               |       |          |       |          |  |  |  |
| Chloroform                | nd    |          | nd    |               | nd    |          | nd    |               | 0.050 | 0.001    | 0.088 | 0.003         | 0.027 | 0.00     | 0.111 | 0.007         | 0.046 | 0.002    | 0.027 | 0.0            | bdl   |          | 0.012 | 0.00          | bdl   |          | bdl   |               | 0.012 | 0.00     | 0.015 | 0.00     |  |  |  |
| Bromodichloromethane      | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |               | 0.027 | 0.0      | 0.015 | 0.001         | -     |          | -     |                | 0.013 | 0.00     | 0.008 | 0.00          | -     |          | -     |               | bdl   |          | bdl   |          |  |  |  |
| Dibromochloromethane      | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |                | 0.007 | 0.001    | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |          |  |  |  |
| Bromoform                 | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | 0.042 | 0.002         | -     |          | -     |                | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |          |  |  |  |
| Total THMs                | 0.0   |          | 0.0   |               | 0.0   |          | 0.0   |               | 0.05  |          | 0.09  |               | 0.05  |          | 0.17  |               | 0.05  |          | 0.03  |                | 0.02  |          | 0.02  |               | 0.0   |          | 0.0   |               | 0.01  |          | 0.01  |          |  |  |  |
|                           |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |                |       |          |       |               |       |          |       |               |       |          |       |          |  |  |  |
| Monochloroacetic acid     | 0.30  | 0.00     | 0.69  | 0.06          | 0.34  | 0.05     | 0.64  | 0.04          | 0.09  | 0.01     | 0.18  | 0.02          | 0.61  | 0.14     | 0.06  | 0.00          | 0.14  | 0.00     | 0.46  | 0.04           | 0.077 | 0.00     | 0.48  | 0.07          | 0.051 | 0.009    | 0.13  | 0.003         | 0.06  | 0.14     | 0.12  | 0.07     |  |  |  |
| Monobromoacetic acid      | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |                | 0.015 | 0.001    | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |          |  |  |  |
| Dichloroacetic acid       | 0.018 | 0.001    | bdl   |               | 0.016 | 0.002    | bdl   |               | 0.048 | 0.003    | 0.227 | 0.017         | 0.036 | 0.004    | bdl   |               | bdl   |          | bdl   |                | bdl   |          | bdl   |               | bdl   |          | bdl   |               | 0.028 | 0.01     | bdl   |          |  |  |  |
| Trichloroacetic acid      | bdl   |          | bdl   |               | bdl   |          | bdl   |               | bdl   |          | 0.376 | 0.055         | bdl   |          | bdl   |               | bdl   |          | bdl   |                | bdl   |          | bdl   |               | bdl   |          | 0.117 | 0.007         | bdl   |          | bdl   |          |  |  |  |
| Dibromoacetic acid        | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |                | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |          |  |  |  |
| Bromochloroacetic acid    | -     |          | -     |               | 0.029 | 0.002    | 0.030 | 0.003         | -     |          | -     |               | bdl   |          | 0.038 | 0.006         | -     |          | -     |                | 0.041 | 0.02     | 0.033 | 0.012         | -     |          | -     |               | 0.036 | 0.001    | 0.045 | 0.001    |  |  |  |
| Bromodichloroacetic acid  | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |                | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | bdl   |          |  |  |  |
| Dibromochloroacetic acid  | -     |          | -     |               | bdl   |          | bdl   | 0.001         | -     |          | -     |               | 0.013 | 0.007    | bdl   |               | -     |          | -     |                | 0.008 | 0.002    | 0.010 | 0.003         | -     |          | -     |               | bdl   |          | 0.010 | 0.000    |  |  |  |
| Trihaloacetic acid        | -     |          | -     |               | 0.017 | 0.002    | 0.011 | 0.001         | -     |          | -     |               | 0.019 | 0.008    | 0.011 | 0.003         | -     |          | -     |                | bdl   |          | 0.008 | 0.001         | -     |          | -     |               | 0.009 |          | 0.014 | 0.001    |  |  |  |
| Total HAAs                | 0.3   |          | 0.7   |               | 0.4   |          | 0.7   |               | 0.1   |          | 0.8   |               | 0.7   |          | 0.1   |               | 0.1   |          | 0.5   |                | 0.1   |          | 0.5   |               | 0.1   |          | 0.2   |               | 0.1   |          | 0.2   |          |  |  |  |
|                           |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |                |       |          |       |               |       |          |       |               |       |          |       |          |  |  |  |
| Monochloroacetonitrile    | nd    |          | nd    |               | nd    |          | nd    |               | nd    |          | nd    |               | nd    |          | nd    |               | nd    |          | nd    |                | nd    |          | nd    |               | nd    |          | nd    |               | nd    |          | nd    |          |  |  |  |
| Monobromoacetonitrile     | -     |          | -     |               | nd    |          | nd    |               | -     |          | -     |               | nd    |          | nd    |               | -     |          | -     |                | nd    |          | nd    |               | -     |          | -     |               | nd    |          | nd    |          |  |  |  |
| Dichloroacetonitrile      | nd    |          | nd    |               | nd    |          | nd    |               | nd    |          | 0.031 | 0.001         | nd    |          | nd    |               | nd    |          | nd    |                | nd    |          | nd    |               | nd    |          | bdl   |               | nd    |          | nd    |          |  |  |  |
| Trichloroacetonitrile     | nd    |          | nd    |               | nd    |          | nd    |               | nd    |          | 0.055 | 0.000         | nd    |          | 0.028 | 0.003         | nd    |          | nd    |                | 0.13  | 0.00     | 0.14  | 0.00          | nd    |          | bdl   |               | nd    |          | nd    |          |  |  |  |
| Dibromoacetonitrile       | -     |          | -     |               | nd    |          | nd    |               | -     |          | -     |               | nd    |          | nd    |               | -     |          | -     |                | nd    |          | nd    |               | -     |          | -     |               | nd    |          | nd    |          |  |  |  |
| Bromochloroacetonitrile   | -     |          | -     |               | nd    |          | nd    |               | -     |          | -     |               | 0.066 | 0.000    | 0.025 | 0.002         | -     |          | -     |                | 0.045 | 0.005    | nd    |               | -     |          | -     |               | nd    |          | nd    |          |  |  |  |
| Dibromochloroacetonitrile | -     |          | -     |               | nd    |          | nd    |               | -     |          | -     |               | nd    |          | nd    |               | -     |          | -     |                | nd    |          | nd    |               | -     |          | -     |               | nd    |          | nd    |          |  |  |  |
| Total HANs                | 0.0   |          | 0.0   |               | 0.0   |          | 0.0   |               | 0.0   |          | 0.1   |               | 0.1   |          | 0.1   |               | 0.0   |          | 0.0   |                | 0.2   |          | 0.1   |               | 0.0   |          | 0.0   |               | 0.0   |          | 0.0   |          |  |  |  |
|                           |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |               |       |          |       |                |       |          |       |               |       |          |       |               |       |          |       |          |  |  |  |
| Monochloroacetamide       | nd    | -        | nd    | -             | nd    | -        | nd    | -             | nd    | -        | nd    | -             | nd    | -        | nd    | -             | nd    | -        | nd    | -              | nd    | -        | nd    | -             | nd    | -        | nd    | -             | nd    | -        | nd    | -        |  |  |  |
| Monobromoacetamide        | -     |          | -     |               | bdl   |          | bdl   |               | -     |          | -     |               | bdl   | 0.00     | 0.05  | 0.00          | -     |          | -     |                | bdl   |          | bdl   |               | -     |          | -     |               | bdl   |          | 0.03  | 0.01     |  |  |  |
| Dichloroacetamide         | 0.067 | 0.000    | 0.061 | 0.000         | 0.084 | 0.033    | bdl   |               | 0.034 | 0.008    | 0.045 | 0.009         | 0.04  | 0.00     | 0.02  | 0.00          | bdl   |          | bdl   |                | bdl   |          | 0.03  | 0.00          | bdl   |          | 0.043 | 0.011         | bdl   |          | 0.03  | 0.00     |  |  |  |
| Trichloroacetamide        | bdl   |          | bdl   |               | bdl   |          | bdl   |               | 0.022 | 0.000    | bdl   |               | 0.02  | 0.01     | 0.05  | 0.01          | bdl   |          | bdl   |                | 0.04  | 0.01     | 0.03  | 0.01          | bdl   |          | 0.026 | 0.002         | bdl   |          | 0.02  | 0.00     |  |  |  |
| Dibromoacetamide          | -     |          | -     |               | 0.40  | 0.05     | 0.065 | 0.01          | -     |          | -     |               | 0.04  | 0.00     | 0.33  | 0.01          | -     |          | -     |                | 0.28  | 0.03     | 0.03  | 0.00          | -     |          | -     |               | 0.06  | 0.01     | 0.31  | 0.03     |  |  |  |
| Bromochloroacetamide      | -     |          | -     |               | 0.20  | 0.03     | 0.272 | 0.03          | -     |          | -     |               | bdl   |          | 0.03  | 0.00          | -     |          | -     |                | 0.04  | 0.03     | 0.05  | 0.01          | -     |          | -     |               | 0.07  | 0.04     | 0.04  | 0.01     |  |  |  |
| Bromodichloroacetamide    | -     |          | -     |               | 0.04  | 0.00     | 0.056 | 0.02          | -     |          | -     |               | 0.02  | 0.01     | 0.02  | 0.00          | -     |          | -     |                | bdl   |          | 0.03  | 0.01          | -     |          | -     |               | 0.03  | 0.02     | 0.05  | 0.00     |  |  |  |
| Dibromochloroacetamide    | -     |          | -     |               | 0.38  | 0.07     | 0.493 | 0.13          | -     |          | -     |               | 0.09  | 0.01     | 0.22  | 0.01          | -     |          | -     |                | 0.19  | 0.02     | 0.20  | 0.00          | -     |          | -     |               | 0.24  | 0.01     | 0.19  | 0.04     |  |  |  |
| Trihaloacetamide          | -     |          | -     |               | 0.06  | 0.01     | 0.133 | 0.03          | -     |          | -     |               | 0.05  | 0.02     | 0.03  | 0.00          | -     |          | -     |                | 0.03  | 0.00     | 0.03  | 0.00          | -     |          | -     |               | 0.04  | 0.00     | 0.03  | 0.01     |  |  |  |
| Total HAcs                | 0.1   |          | 0.1   |               | 1.2   |          | 1.0   |               | 0.1   |          | 0.0   |               | 0.3   |          | 0.7   |               | 0.0   |          | 0.0   |                | 0.6   |          | 0.4   |               | 0.0   |          | 0.1   |               | 0.4   |          | 0.7   |          |  |  |  |

**Table E. 4:** Raw data of chlorinated and chloraminated **acrylamide** (screening and detailed phase).

| Acrylamide                |      | Chlorination |          |             |          |             |          |             |          |             |          |             |          |               |          |             |          | Chloramination |          |             |          |             |          |             |          |             |          |             |          |             |          |             |          |
|---------------------------|------|--------------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|---------------|----------|-------------|----------|----------------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|
|                           |      | pH 7         |          |             |          |             |          |             |          | pH 8        |          |             |          |               |          |             |          | pH 7           |          |             |          |             |          |             |          | pH 8        |          |             |          |             |          |             |          |
|                           |      | -            |          |             |          | with Br-    |          |             |          | -           |          |             |          | with Br-      |          |             |          | -              |          |             |          | with Br-    |          |             |          | -           |          |             |          | with Br-    |          |             |          |
|                           |      | 4 h          |          | 24 h        |          | 4 h         |          | 24 h        |          | 4 h         |          | 24 h        |          | 4 h           |          | 24 h        |          | 4 h            |          | 24 h        |          | 4 h         |          | 24 h        |          | 4 h         |          | 24 h        |          | 4 h         |          | 24 h        |          |
|                           |      | Molar yield  | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. | Concentration | std dev. | Molar yield | std dev. | Molar yield    | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. |
| DBPs                      |      | Units        |          |             |          |             |          |             |          |             |          |             |          |               |          |             |          |                |          |             |          |             |          |             |          |             |          |             |          |             |          |             |          |
| Chloroform                | nd   |              | nd       |             | nd       |             | nd       |             | 0.104    | 0.01        | 0.086    | 0.00        | 0.097    | 0.004         | 0.16     | 0.04        | 0.067    | 0.002          | 0.049    | 0.008       | bdl      |             | 0.010    | 0.001       | bdl      |             | bdl      |             | 0.009    | 0.000       | 0.013    | 0.01        |          |
| Bromodichloromethane      | -    |              | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |               | 0.11     | -           | -        |                | -        |             | 0.012    |             | bdl      |             | -        |             | -        |             | bdl      |             | 0.0070   | 0.0042      |          |
| Dibromochloromethane      | -    |              | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | 0.013    | 0.000         | bdl      |             | -        |                | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |             | bdl      |             |          |
| Bromoform                 | -    |              | -        |             | bdl      |             | 0.103    | 0.01        | -        |             | -        |             | bdl      |               | 0.07     | -           | -        |                | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |             | bdl      |             |          |
| Total THMs                | 0.0  |              | 0.0      |             | 0.0      |             | 0.1      |             | 0.1      |             | 0.1      |             | 0.1      |               | 0.3      |             | 0.1      |                | 0.0      |             | 0.0      |             | 0.0      |             | 0.0      |             | 0.0      |             | 0.009    |             | 0.020    |             |          |
| HAAs                      |      | M/M %        |          |             |          |             |          |             |          |             |          |             |          |               |          |             |          |                |          |             |          |             |          |             |          |             |          |             |          |             |          |             |          |
| Monochloroacetic acid     | 0.64 | 0.001        | 0.46     | 0.038       | 0.570    | 0.01        | 0.276    | 0.024       | 0.532    | 0.076       | bdl      |             | 0.689    | 0.03          | 0.409    | 0.010       | 0.26     | 0.05           | 0.32     | 0.010       | 0.25     | 0.08        | 0.30     | 0.026       | 0.076    | 0.02        | 0.127    | 0.003       | 0.093    | 0.003       | 0.150    | 0.036       |          |
| Monobromoacetic acid      | -    |              | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |               | bdl      |             | -        |                | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |             | bdl      |             |          |
| Dichloroacetic acid       | bdl  |              | bdl      |             | bdl      |             | 0.030    | 0.010       | 0.040    | 0.015       | 0.26     | 0.19        | 0.055    | 0.017         | bdl      |             | bdl      |                | bdl      |             | bdl      |             | bdl      |             | bdl      |             | bdl      |             | bdl      |             | bdl      |             |          |
| Trichloroacetic acid      | bdl  |              | bdl      |             | bdl      |             | bdl      |             | bdl      |             | 0.15     | 0.02        | bdl      |               | bdl      |             | bdl      |                | bdl      |             | bdl      |             | bdl      |             | bdl      |             | 0.115    | 0.003       | bdl      |             | bdl      |             |          |
| Dibromoacetic acid        | -    |              | -        |             | bdl      |             | 0.011    | 0.000       | -        |             | -        |             | bdl      |               | bdl      |             | -        |                | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |             | bdl      |             |          |
| Bromochloroacetic acid    | -    |              | -        |             | 0.037    | 0.005       | 0.042    | 0.001       | -        |             | -        |             | bdl      |               | 0.040    | 0.004       | -        |                | -        |             | 0.024    | 0.004       | 0.034    | 0.010       | -        |             | -        |             | 0.040    | 0.013       | 0.034    | 0.011       |          |
| Bromodichloroacetic acid  | -    |              | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |               | bdl      |             | -        |                | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |             | bdl      |             |          |
| Dibromochloroacetic acid  | -    |              | -        |             | bdl      |             | 0.010    | -           | -        |             | -        |             | 0.027    | 0.014         | bdl      |             | -        |                | -        |             | 0.010    | 0.003       | 0.011    | 0.003       | -        |             | -        |             | bdl      |             | bdl      |             |          |
| Trihaloacetic acid        | -    |              | -        |             | 0.014    | 0.003       | 0.012    | 0.003       | -        |             | -        |             | 0.017    | 0.004         | 0.011    | 0.002       | -        |                | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | 0.017    | 0.001       | 0.010    | 0.000       |          |
| Total HAAs                | 0.6  |              | 0.5      |             | 0.6      |             | 0.4      |             | 0.6      |             | 0.4      |             | 0.8      |               | 0.5      |             | 0.3      |                | 0.3      |             | 0.3      |             | 0.3      |             | 0.1      |             | 0.2      |             | 0.1      |             | 0.2      |             |          |
| HANs                      |      | M/M %        |          |             |          |             |          |             |          |             |          |             |          |               |          |             |          |                |          |             |          |             |          |             |          |             |          |             |          |             |          |             |          |
| Monochloroacetonitrile    | nd   |              | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |               | nd       |             | nd       |                | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             |          |
| Monobromoacetonitrile     | -    |              | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |               | nd       |             | -        |                | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |             | nd       |             |          |
| Dichloroacetonitrile      | nd   |              | nd       |             | nd       |             | nd       |             | nd       |             | 0.029    | 0.001       | nd       |               | nd       |             | nd       |                | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             |          |
| Trichloroacetonitrile     | nd   |              | nd       |             | nd       |             | nd       |             | nd       |             | 0.087    | 0.016       | nd       |               | 0.11     | 0.000       | nd       |                | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             |          |
| Dibromoacetonitrile       | -    |              | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |               | nd       |             | -        |                | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |             | nd       |             |          |
| Bromochloroacetonitrile   | -    |              | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |               | nd       |             | -        |                | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |             | nd       |             |          |
| Dibromochloroacetonitrile | -    |              | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |               | nd       |             | -        |                | -        |             | nd       |             | nd       |             | -        |             | -        |             | nd       |             | nd       |             |          |
| Total HANs                | 0.0  |              | 0.0      |             | 0.0      |             | 0.0      |             | 0.0      |             | 0.12     |             | 0.0      |               | 0.11     |             | 0.0      |                | 0.0      |             | 0.0      |             | 0.0      |             | 0.0      |             | 0.0      |             | 0.0      |             | 0.0      |             |          |
| HAcAms                    |      | M/M %        |          |             |          |             |          |             |          |             |          |             |          |               |          |             |          |                |          |             |          |             |          |             |          |             |          |             |          |             |          |             |          |
| Monochloroacetamide       | nd   |              | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |               | nd       |             | nd       |                | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             | nd       |             |          |
| Monobromoacetamide        | -    |              | -        |             | bdl      |             | 0.18     | 0.01        | -        |             | -        |             | 0.02     | 0.01          | 0.05     | 0.00        | -        |                | -        |             | bdl      |             | bdl      |             | -        |             | -        |             | bdl      |             | 0.04     | 0.02        |          |
| Dichloroacetamide         | bdl  |              | bdl      |             | bdl      |             | 0.45     | 0.03        | 0.16     | 0.08        | 0.04     | 0.00        | 0.03     | 0.00          | 0.02     | 0.01        | 0.050    | 0.007          | 0.038    | 0.008       | bdl      |             | 0.02     | 0.01        | bdl      |             | 0.15     | 0.01        | bdl      |             | 0.03     | 0.01        |          |
| Trichloroacetamide        | bdl  |              | bdl      |             | 0.03     | 0.00        | bdl      |             | 0.20     | 0.03        | bdl      |             | 0.04     | 0.00          | 0.04     | 0.00        | bdl      |                | bdl      |             | 0.03     | 0.01        | bdl      | 0.008       | bdl      |             | 0.01     | 0.00        | bdl      |             | bdl      |             |          |
| Dibromoacetamide          | -    |              | -        |             | 0.60     | 0.09        | 0.52     | 0.00        | -        |             | -        |             | 0.09     | 0.00          | 0.32     | 0.03        | -        |                | -        |             | 0.31     | 0.04        | 0.27     | 0.02        | -        |             | -        |             | 0.04     | 0.02        | 0.30     | 0.02        |          |
| Bromochloroacetamide      | -    |              | -        |             | 0.33     | 0.01        | 0.24     | 0.01        | -        |             | -        |             | 0.01     | 0.00          | 0.06     | 0.02        | -        |                | -        |             | 0.08     | 0.03        | 0.04     | 0.00        | -        |             | -        |             | 0.05     | 0.03        | 0.03     | 0.01        |          |
| m-Bromodichloroacetamide  | -    |              | -        |             | 0.12     | 0.01        | 0.06     | 0.03        | -        |             | -        |             | bdl      |               | 0.03     | 0.01        | -        |                | -        |             | 0.02     | 0.00        | 0.03     | 0.01        | -        |             | -        |             | 0.03     | 0.00        | 0.02     | 0.01        |          |
| m-Dibromochloroacetamide  | -    |              | -        |             | 0.61     | 0.19        | 0.46     | 0.02        | -        |             | -        |             | 0.39     | 0.04          | 0.21     | 0.02        | -        |                | -        |             | 0.21     | 0.03        | 0.18     | 0.01        | -        |             | -        |             | 0.19     | 0.04        | 0.18     | 0.01        |          |
| Trihaloacetamide          | -    |              | -        |             | 0.19     | 0.27        | 0.12     | 0.01        | -        |             | -        |             | -        | 0.02          | 0.00     | 0.03        | 0.00     | -              |          | -           |          | 0.03        | 0.00     | 0.03        | 0.00     | -           |          | -           |          | 0.03        | 0.01     | 0.02        | 0.00     |
| Total HAcAms              | 0.0  |              | 0.0      |             | 1.9      |             | 2.0      |             | 0.4      |             | 0.0      |             | 0.6      |               | 0.8      |             | 0.0      |                | 0.0      |             | 0.7      |             | 0.6      |             | 0.0      |             | 0.2      |             | 0.3      |             | 0.6      |             |          |

**Table E. 5:** Raw data of chlorinated and chloraminated  **$\beta$ -alaninamide** (screening and detailed phase).

| <b><math>\beta</math>-Alaninamide</b> |                           | Chlorination |          |             |          |              |          |              |          | Chloramination |          |             |          |             |          |             |          |
|---------------------------------------|---------------------------|--------------|----------|-------------|----------|--------------|----------|--------------|----------|----------------|----------|-------------|----------|-------------|----------|-------------|----------|
|                                       |                           | pH 7         |          |             |          | pH 8         |          |              |          | pH 7           |          |             |          | pH 8        |          |             |          |
|                                       |                           | -            |          | with Br-    |          | -            |          | with Br-     |          | -              |          | with Br-    |          | -           |          | with Br-    |          |
|                                       |                           | 4 h          | 24 h     | 4 h         | 24 h     | 4 h          | 24 h     | 4 h          | 24 h     | 4 h            | 24 h     | 4 h         | 24 h     | 4 h         | 24 h     | 4 h         | 24 h     |
|                                       |                           | Molar yield  | std dev. | Molar yield | std dev. | Molar yield  | std dev. | Molar yield  | std dev. | Molar yield    | std dev. | Molar yield | std dev. | Molar yield | std dev. | Molar yield | std dev. |
| <b>DBPs</b>                           | <b>Units</b>              |              |          |             |          |              |          |              |          |                |          |             |          |             |          |             |          |
| CHCl <sub>3</sub>                     | Chloroform                | nd           |          | nd          |          | nd           |          | 0.20         | 0.01     | 0.28           | 0.02     | 0.37        | 0.02     | 0.23        | 0.04     | bdl         |          |
| CHBrCl <sub>2</sub>                   | Bromodichloromethane      | -            |          | bdl         |          | bdl          |          | -            |          | -              |          | bdl         |          | 0.13        | 0.05     | -           |          |
| CHBr <sub>2</sub> Cl                  | Dibromochloromethane      | -            |          | bdl         |          | bdl          |          | -            |          | 0.06           | 0.004    | 0.029       |          | -           |          | -           |          |
| CHBr <sub>3</sub>                     | Bromoform                 | -            |          | bdl         |          | bdl          |          | -            |          | bdl            |          | 0.046       | 0.01     | -           |          | -           |          |
| <b>Total THMs</b>                     |                           | <b>0.0</b>   |          | <b>0.0</b>  |          | <b>0.0</b>   |          | <b>0.2</b>   |          | <b>0.3</b>     |          | <b>0.43</b> |          | <b>0.43</b> |          | <b>0.0</b>  |          |
| MCAA                                  | Monochloroacetic acid     | 0.46         | 0.03     | 0.70        | 0.02     | 0.42         | 0.07     | 0.52         | 0.07     | 0.240          | 0.032    | -           | 0.05     | 0.36        | 0.07     | 0.08        | 0.001    |
| MBAA                                  | Monobromoacetic acid      | -            |          | bdl         |          | bdl          |          | -            |          | bdl            |          | bdl         |          | -           |          | -           |          |
| DCAA                                  | Dichloroacetic acid       | bdl          |          | bdl         |          | bdl          |          | 0.024        | 0.004    | 0.133          | 0.01     | 0.043       | 0.021    | bdl         |          | bdl         |          |
| TCAA                                  | Trichloroacetic acid      | bdl          |          | bdl         |          | bdl          |          | bdl          |          | 0.233          | 0.07     | bdl         |          | bdl         |          | bdl         |          |
| DBAA                                  | Dibromoacetic acid        | -            |          | -           |          | bdl          |          | -            |          | -              |          | bdl         |          | -           |          | -           |          |
| BCAA                                  | Bromochloroacetic acid    | -            |          | 0.025       | 0.004    | 0.042        | 0.02     | -            |          | 0.025          | 0.001    | 0.032       | 0.004    | -           |          | -           |          |
| BDCAA                                 | Bromodichloroacetic acid  | -            |          | bdl         |          | bdl          |          | -            |          | bdl            |          | bdl         |          | -           |          | -           |          |
| DBCAA                                 | Dibromochloroacetic acid  | -            |          | bdl         |          | 0.008        | 0.000    | -            |          | 0.014          | 0.007    | bdl         |          | -           |          | -           |          |
| TBAA                                  | Tribromoacetic acid       | -            |          | 0.010       | 0.000    | 0.013        | 0.001    | -            |          | 0.020          | 0.003    | 0.011       | 0.002    | -           |          | -           |          |
| <b>Total HAAs</b>                     |                           | <b>0.5</b>   |          | <b>0.7</b>  |          | <b>0.459</b> |          | <b>0.579</b> |          | <b>0.3</b>     |          | <b>0.4</b>  |          | <b>0.5</b>  |          | <b>0.1</b>  |          |
| MCAN                                  | Monochloroacetonitrile    | nd           |          | nd          |          | nd           |          | nd           |          | nd             |          | nd          |          | nd          |          | nd          |          |
| MBAN                                  | Monobromoacetonitrile     | -            |          | nd          |          | nd           |          | -            |          | nd             |          | nd          |          | -           |          | -           |          |
| DCAN                                  | Dichloroacetonitrile      | nd           |          | nd          |          | nd           |          | 0.027        | 0.00     | nd             |          | nd          |          | nd          |          | nd          |          |
| TCAN                                  | Trichloroacetonitrile     | nd           |          | nd          |          | nd           |          | 0.046        | 0.01     | nd             |          | nd          |          | nd          |          | nd          |          |
| DBAN                                  | Dibromoacetonitrile       | -            |          | nd          |          | nd           |          | -            |          | nd             |          | nd          |          | -           |          | -           |          |
| BCAN                                  | Bromochloroacetonitrile   | -            |          | nd          |          | nd           |          | -            |          | nd             |          | nd          |          | -           |          | -           |          |
| DBCAN                                 | Dibromochloroacetonitrile | -            |          | nd          |          | nd           |          | -            |          | nd             |          | nd          |          | -           |          | -           |          |
| <b>Total HANs</b>                     |                           | <b>0.0</b>   |          | <b>0.0</b>  |          | <b>0.0</b>   |          | <b>0.0</b>   |          | <b>0.1</b>     |          | <b>0.0</b>  |          | <b>0.0</b>  |          | <b>0.0</b>  |          |
| MCACAm                                | Monochloroacetamide       | nd           |          | nd          |          | nd           |          | nd           |          | nd             |          | nd          |          | nd          |          | nd          |          |
| MBACAm                                | Monobromoacetamide        | -            |          | bdl         |          | bdl          |          | -            |          | 0.07           | 0.02     | 0.05        | 0.00     | -           |          | -           |          |
| DCACAm                                | Dichloroacetamide         | 0.19         | 0.08     | 1.32        | 0.086    | bdl          |          | 0.036        | 0.001    | 0.064          | 0.01     | 0.03        | 0.01     | 0.054       | 0.001    | 0.049       | 0.004    |
| TCACAm                                | Trichloroacetamide        | bdl          |          | bdl         |          | 0.02         | 0.01     | bdl          |          | 0.014          | 0.004    | bdl         |          | bdl         |          | bdl         |          |
| DBACAm                                | Dibromoacetamide          | -            |          | 0.42        | 0.04     | 0.63         | 0.02     | -            |          | 0.44           | 0.04     | 0.32        | 0.04     | -           |          | 0.29        | 0.04     |
| BCACAm                                | Bromochloroacetamide      | -            |          | 0.37        | 0.06     | 0.31         | 0.01     | -            |          | 0.01           | 0.01     | 0.07        | 0.01     | -           |          | 0.04        | 0.00     |
| BDCACAm                               | Bromodichloroacetamide    | -            |          | 0.02        | 0.00     | 0.08         | 0.01     | -            |          | bdl            |          | 0.03        | 0.00     | -           |          | 0.01        | 0.00     |
| DBCACAm                               | Dibromochloroacetamide    | -            |          | 0.41        | 0.02     | 0.52         | 0.02     | -            |          | 0.41           | 0.02     | 0.22        | 0.02     | -           |          | 0.19        | 0.03     |
| TBACAm                                | Tribromoacetamide         | -            |          | 0.06        | 0.00     | 0.13         | 0.01     | -            |          | 0.19           | 0.01     | 0.03        | 0.00     | -           |          | 0.03        | 0.00     |
| <b>Total HACams</b>                   |                           | <b>0.2</b>   |          | <b>1.3</b>  |          | <b>1.3</b>   |          | <b>1.7</b>   |          | <b>0.1</b>     |          | <b>0.1</b>  |          | <b>1.2</b>  |          | <b>0.8</b>  |          |

**Table E. 6:** Raw data of chlorinated and chloraminated **hydroxybenzamide** (screening and detailed phase).

| Hydroxybenzamide          |       | Chlorination |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         | Chloramination |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
|---------------------------|-------|--------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|----------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|-------------|---------|
|                           |       | pH 7         |         |             |         |             |         |             |         | pH 8        |         |             |         |             |         |             |         | pH 7           |         |             |         |             |         |             |         | pH 8        |         |             |         |             |         |             |         |
|                           |       | -            |         |             |         | with Br-    |         |             |         | -           |         |             |         | with Br-    |         |             |         | -              |         |             |         | with Br-    |         |             |         | -           |         |             |         | with Br-    |         |             |         |
|                           |       | 4 h          |         | 24 h        |         | 4 h         |         | 24 h        |         | 4 h         |         | 24 h        |         | 4 h         |         | 24 h        |         | 4 h            |         | 24 h        |         | 4 h         |         | 24 h        |         | 4 h         |         | 24 h        |         | 4 h         |         | 24 h        |         |
|                           |       | Molar yield  | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield    | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev | Molar yield | std dev |
| DBPs                      | Units |              |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |                |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
| Chloroform                | nd    | nd           | nd      | nd          | 0.23    | 0.005       | 0.14    | 0.000       | 0.276   | 0.006       | 0.307   | 0.035       | bdl     | bdl         | 0.11    | 0.01        | 0.09    | 0.01           | bdl     | bdl         | 0.13    | 0.02        | 0.150   | 0.000       |         |             |         |             |         |             |         |             |         |
| Bromodichloromethane      | -     | -            | bdl     | bdl         | -       | -           | -       | -           | bdl     | 0.136       | 0.004   | -           | -       | 0.07        | 0.02    | 0.20        | 0.06    | -              | -       | bdl         | 0.016   | 0.009       |         |             |         |             |         |             |         |             |         |             |         |
| Dibromochloromethane      | -     | -            | bdl     | bdl         | -       | -           | -       | -           | 0.606   | 0.14        | 0.259   | -           | -       | 0.11        | -       | 0.110       | 0.01    | -              | -       | bdl         | 0.017   | 0.003       |         |             |         |             |         |             |         |             |         |             |         |
| Bromoform                 | -     | -            | bdl     | bdl         | -       | -           | -       | -           | bdl     | 0.207       | 0.014   | -           | -       | 0.08        | -       | 0.175       | 0.04    | -              | -       | bdl         | 0.081   | 0.006       |         |             |         |             |         |             |         |             |         |             |         |
| Total THMs                | 0.0   | 0.0          | 0.0     | 0.0         | 0.2     | 0.1         | 0.88    | 0.91        | 0.0     | 0.0         | 0.4     | 0.6         | 0.0     | 0.0         | 0.134   | 0.264       |         |                |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
|                           |       |              |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |                |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
| Monochloroacetic acid     | 1.05  | 0.24         | 0.51    | 0.09        | 0.60    | 0.004       | 0.50    | 0.009       | 0.155   | 0.022       | 0.068   | 0.009       | 0.26    | 0.04        | 0.40    | 0.007       | 0.51    | 0.04           | 0.53    | 0.09        | 0.360   | 0.008       | 0.59    | 0.070       | 0.180   | 0.005       | 0.141   | 0.044       | 0.060   | 0.012       | bdl     |             |         |
| Monobromoacetic acid      | -     | -            | bdl     | bdl         | -       | -           | -       | -           | bdl     | 0.014       | 0.000   | bdl         | bdl     | 0.028       | 0.004   | bdl         | bdl     | bdl            | bdl     | bdl         | bdl     | bdl         | bdl     |             |         |             |         |             |         |             |         |             |         |
| Dichloroacetic acid       | bdl   | bdl          | 0.015   | 0.001       | 0.030   | 0.002       | 0.021   | 0.002       | bdl     | 0.021       | 0.001   | bdl         | bdl     | bdl         | bdl     | bdl         | bdl     | bdl            | bdl     | bdl         | bdl     | bdl         |         |             |         |             |         |             |         |             |         |             |         |
| Trichloroacetic acid      | bdl   | bdl          | bdl     | bdl         | bdl     | bdl         | bdl     | bdl         | bdl     | bdl         | bdl     | bdl         | -       | -           | bdl     | bdl         | -       | -              | bdl     | bdl         | bdl     | bdl         |         |             |         |             |         |             |         |             |         |             |         |
| Dibromoacetic acid        | -     | -            | -       | -           | -       | -           | -       | -           | -       | -           | -       | -           | -       | -           | -       | -           | -       | -              | -       | -           | -       | -           |         |             |         |             |         |             |         |             |         |             |         |
| Bromochloroacetic acid    | -     | -            | 0.027   | 0.002       | 0.043   | 0.001       | -       | -           | 0.030   | 0.006       | bdl     | bdl         | -       | -           | 0.034   | 0.007       | 0.038   | 0.003          | -       | -           | 0.048   | 0.002       | 0.044   |             |         |             |         |             |         |             |         |             |         |
| Bromodichloroacetic acid  | -     | -            | bdl     | bdl         | -       | -           | -       | -           | bdl     | bdl         | -       | -           | bdl     | bdl         | -       | -           | bdl     | bdl            | -       | -           | bdl     | bdl         |         |             |         |             |         |             |         |             |         |             |         |
| Dibromochloroacetic acid  | -     | -            | bdl     | bdl         | -       | -           | -       | -           | 0.010   | 0.000       | bdl     | bdl         | -       | -           | 0.008   | 0.003       | bdl     | bdl            | -       | -           | 0.020   | 0.008       | 0.011   |             |         |             |         |             |         |             |         |             |         |
| Trihaloacetic acid        | -     | -            | 0.010   | 0.002       | 0.012   | 0.001       | -       | -           | 0.016   | 0.000       | 0.010   | 0.001       | -       | -           | 0.029   | 0.001       | 0.006   | 0.001          | -       | -           | 0.026   | 0.004       | 0.009   | 0.000       |         |             |         |             |         |             |         |             |         |
| Total HAAs                | 1.0   | 0.5          | 0.7     | 0.6         | 0.2     | 0.1         | 0.3     | 0.4         | 0.5     | 0.5         | 0.5     | 0.6         | 0.2     | 0.1         | 0.2     | 0.1         |         |                |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
|                           |       |              |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |                |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
| Monochloroacetonitrile    | nd    | nd           | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd             | nd      | nd          | nd      | nd          |         |             |         |             |         |             |         |             |         |             |         |
| Monobromoacetonitrile     | -     | -            | nd      | nd          | -       | -           | nd      | nd          | nd      | -           | -       | nd          | nd      | -           | -       | nd          | nd      | -              | -       | nd          | nd      |             |         |             |         |             |         |             |         |             |         |             |         |
| Dichloroacetonitrile      | nd    | nd           | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd             | nd      | nd          | nd      |             |         |             |         |             |         |             |         |             |         |             |         |
| Trichloroacetonitrile     | nd    | nd           | nd      | nd          | nd      | 0.137       | 0.001   | nd          | nd      | 0.17        | nd      | 0.137       | 0.13    | 0.01        | nd      | 0.1727      | 0.01    | nd             | nd      | nd          | nd      |             |         |             |         |             |         |             |         |             |         |             |         |
| Dibromoacetonitrile       | -     | -            | nd      | nd          | nd      | nd          | -       | nd          | nd      | -           | -       | nd          | nd      | -           | -       | nd          | nd      | -              | -       | nd          | nd      |             |         |             |         |             |         |             |         |             |         |             |         |
| Bromochloroacetonitrile   | -     | -            | nd      | nd          | -       | -           | nd      | nd          | nd      | -           | -       | 0.028       | 0.020   | 0.006       | -       | -           | nd      | nd             | -       | -           | nd      | nd          |         |             |         |             |         |             |         |             |         |             |         |
| Dibromochloroacetonitrile | -     | -            | nd      | nd          | -       | -           | nd      | nd          | nd      | -           | -       | nd          | nd      | -           | -       | nd          | nd      | -              | -       | nd          | nd      |             |         |             |         |             |         |             |         |             |         |             |         |
| Total HANs                | 0.0   | 0.0          | 0.0     | 0.0         | 0.0     | 0.137       | 0.0     | 0.0         | 0.166   | 0.0         | 0.165   | 0.148       | 0.0     | 0.173       | 0.0     | 0.0         |         |                |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
|                           |       |              |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |                |         |             |         |             |         |             |         |             |         |             |         |             |         |             |         |
| Monochloroacetamide       | nd    | nd           | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd          | nd      | nd             | nd      | nd          | nd      |             |         |             |         |             |         |             |         |             |         |             |         |
| Monobromoacetamide        | -     | -            | bdl     | bdl         | -       | -           | -       | -           | 0.036   | 0.000       | 0.042   | 0.009       | -       | -           | bdl     | -           | -       | -              | -       | 0.017       | 0.004   | 0.036       | 0.002   |             |         |             |         |             |         |             |         |             |         |
| Dichloroacetamide         | 0.45  | 0.17         | bdl     | bdl         | 0.06    | 0.010       | 0.100   | 0.028       | 0.016   | 0.000       | bdl     | bdl         | 0.024   | 0.007       | 0.077   | 0.008       | 0.017   | 0.002          | bdl     | bdl         | 0.029   | 0.002       | 0.036   | 0.006       |         |             |         |             |         |             |         |             |         |
| Trichloroacetamide        | bdl   | bdl          | 0.04    | 0.00        | bdl     | 0.038       | 0.012   | 0.037       | 0.004   | 0.04        | 0.01    | 0.02        | 0.01    | bdl         | 0.01    | 0.00        | bdl     | bdl            | 0.01    | 0.01        | 0.01    | 0.00        | 0.03    | 0.00        |         |             |         |             |         |             |         |             |         |
| Dibromoacetamide          | -     | -            | 0.76    | 0.01        | 0.51    | 0.01        | -       | -           | 0.05    | 0.01        | 0.26    | 0.00        | -       | -           | 0.27    | 0.08        | 0.03    | -              | -       | 0.06        | 0.02    | 0.31        | 0.01    |             |         |             |         |             |         |             |         |             |         |
| Bromochloroacetamide      | -     | -            | 0.44    | 0.05        | 0.24    | 0.05        | -       | -           | 0.02    | 0.00        | 0.03    | 0.00        | -       | -           | 0.03    | 0.00        | 0.04    | 0.00           | -       | 0.04        | 0.01    | 0.02        | 0.01    |             |         |             |         |             |         |             |         |             |         |
| Bromodichloroacetamide    | -     | -            | 0.08    | 0.04        | 0.06    | 0.02        | -       | -           | 0.09    | 0.01        | 0.02    | 0.01        | -       | -           | 0.01    | 0.00        | 0.03    | 0.00           | -       | 0.03        | 0.00    | 0.03        | 0.00    |             |         |             |         |             |         |             |         |             |         |
| Dibromochloroacetamide    | -     | -            | 0.61    | 0.00        | 0.51    | 0.01        | -       | -           | 0.29    | 0.08        | 0.17    | 0.01        | -       | -           | 0.17    | 0.04        | 0.18    | 0.04           | -       | -           | 0.28    | 0.00        | 0.21    | 0.00        |         |             |         |             |         |             |         |             |         |
| Trihaloacetamide          | -     | -            | 0.15    | 0.02        | 0.12    | 0.02        | -       | -           | 0.08    | 0.00        | 0.03    | 0.00        | -       | -           | 0.03    | 0.01        | 0.03    | 0.01           | -       | -           | 0.02    | 0.00        | 0.03    | 0.00        |         |             |         |             |         |             |         |             |         |
| Total HACams              | 0.5   | 0.0          | 2.1     | 1.5         | 0.1     | 0.1         | 0.6     | 0.6         | 0.1     | 0.0         | 0.5     | 0.3         | 0.0     | 0.0         | 0.5     | 0.3         | 0.0     | 0.0            | 0.0     | 0.0         | 0.5     | 0.7         |         |             |         |             |         |             |         |             |         |             |         |

## Appendix F. Mapping Water Age in Distribution

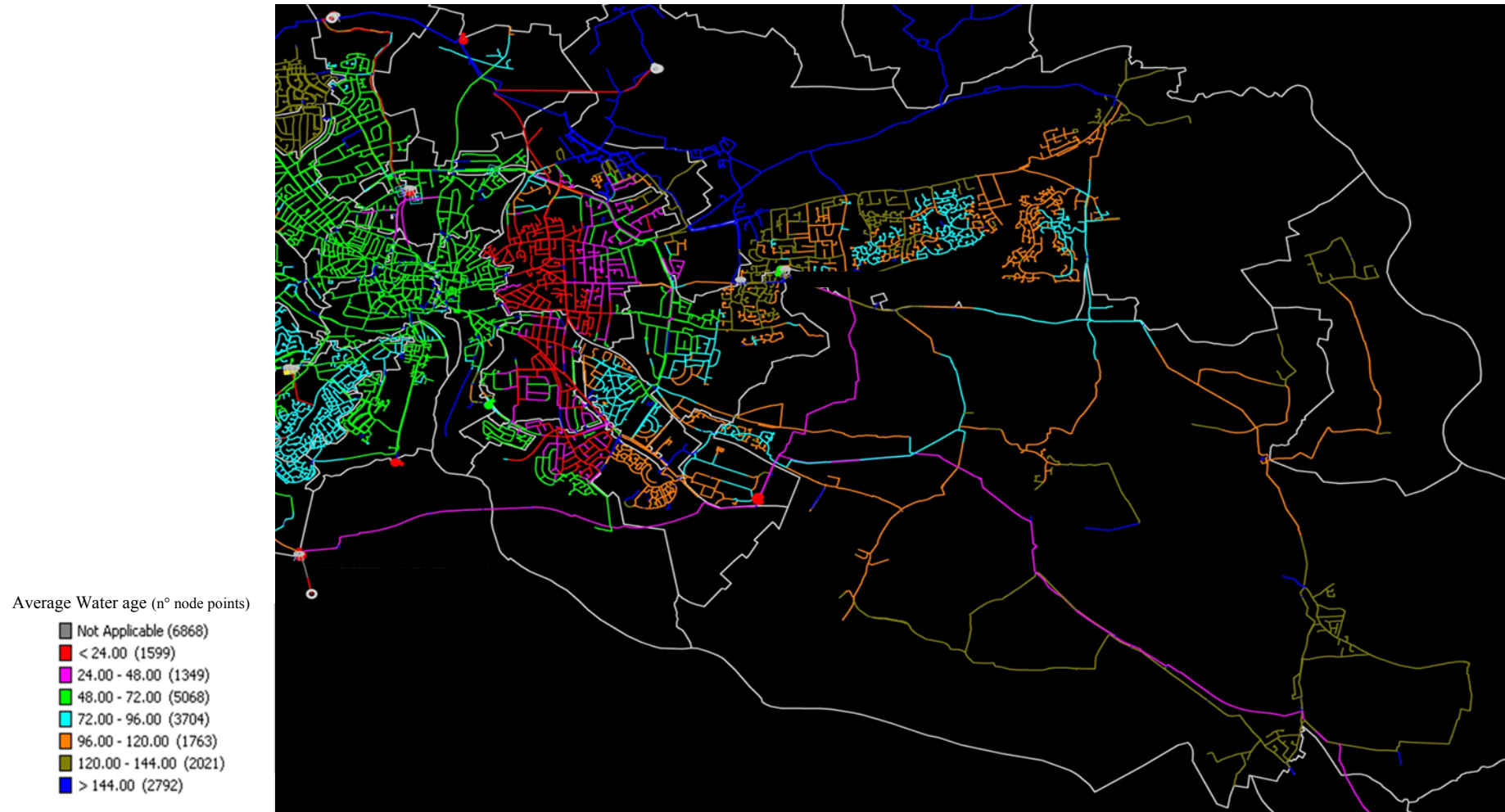


**Figure F. 1:** Example of water age map designed for the purposes of this study (WTW A).