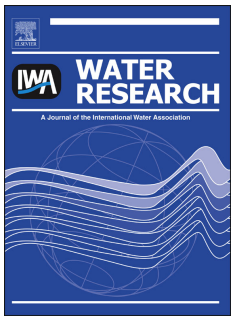
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Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine

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Abstract

The formation of disinfection by-products (DBPs) from chlorination and monochloramination of treated drinking waters was determined. Samples were collected after treatment at 11 water treatment works but before exposure to chlorine or monochloramine. Formation potential tests were carried out to determine the DBPs formed by chlorination and monochloramination. DBPs measured were trihalomethanes (THMs), haloacetic acids (HAAs), halonitromethanes, haloacetonitriles, haloketones and iodo-THMs. All waters had the potential to form significant levels of all the DBPs measured. Compared to chlorine, monochloramination generally resulted in lower concentrations of DBPs with the exception of 1,1-dichloropropanone. The concentrations of THMs correlated well with the HAAs formed. The impact of bromine on the speciation of the DBPs was determined. The literature findings that higher bromide levels lead to higher concentrations of brominated DBPS were confirmed.

Key words: disinfection by-products, trihalomethanes, haloacetic acids, haloacetonitriles, monochloramination, semi-volatile DBPs

Abbreviations

1,1-DCP – 1,1- dichloropropanone

1,1,1-TCP – 1,1,1- trichloropropanone

BCAA – bromochloroacetic acid

BCIM – bromochloroiodomethane

BDCAA – bromodichloroacetic acid

BDCM - bromodichloromethane

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BIF – bromine incorporation factor

CHO – Chinese hamster ovary cells

DBAA – dibromoacetic acid

DBAN –dibromoacetonitrile

DBCAA – dibromochloroacetic acid

DBCM – dibromochloromethane

DBIM – dibromoiodomethane

DBNM – dibromonitromethane

DBPs – disinfection by-products

DCA – dichloroacetaldehyde

DCAA – dichloroacetic acid

DCAN - dichloroacetonitrile

DCBM – dichlorobromomethane

DCIM – dichloroiodomethane

DXAA – dihalogenated acetic acids

FP – formation potential

GC-ECD – gas chromatography electron capture detection

HAs - haloaldehydes

HAAs – haloacetic acids

HANs – haloacetonitriles

HKs – haloketones

HNMs – halonitromethanes

HOBr/OBr^- – hypobromous acid

HOI – hypoiodous acid

ICP/MS – inductively coupled plasma/mass spectrometry

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IO_3^- - iodate

i-THMs – iodo THMs

MXAA – monohalogenated acetic acids

MtBE – methyl tert butyl ether

NaOCl – hypochlorous acid

NOM – natural organic matter

NPOC – non-purgeable organic carbon

SUVA – specific ultraviolet absorbance

TBAA – tribromoacetic acid

TBM – tribromomethane

TCA – trichloroacetaldehyde

TCAA – trichloroacetic acid

TCAN – trichloroacetonitrile

TCM – trichloromethane

TCNM – trichloronitromethane

TXAA – trihalogenated acetic acids

THMs – trihalomethanes

US EPA – United States Environmental Protection Agency

UV – ultraviolet absorbance

Introduction

Drinking water disinfection by-products (DBPs) result from the reaction of disinfectants, such as chlorine or chloramines, with natural organic matter (NOM) and/or bromide/iodide present in drinking water supplies (Rook et al., 1974). Trihalomethanes are the only regulated DBP in the UK and it is required by law that the

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sum of four THMs does not exceed 100 µg L^{-1} with a frequency of sampling dependent on the population size. Haloacetic acids (HAAs) are often found to be as prevalent as THMs but are currently not regulated in the UK. However, the European Union is considering regulating the nine HAAs at 80 µg L^{-1} (Cortvriend, 2008) and as such there is growing interest in the levels of these compounds found in UK drinking waters and how best to control them . In order to comply with these proposed regulations, there has been an increasing interest in using monochloramine as a secondary disinfectant because of reduced DBP formation and its ability to provide residuals in water distribution systems. Monochloramine is known to only form trace amounts of THMs and HAAs, but the formation of dihalogenated HAAs (DXAAs), although generally lower than with chlorine, can still reach significant levels depending on the dose, chlorine to ammonia ratio, pH and other conditions (Diehl et al., 2000; Hua and Reckhow, 2007). The use of monochloramine may also lead to an increase in other DBPs such as haloacetonitriles (HANs) and iodo- THMs (i-THMs) (Krasner et al., 1989; Bichsel and Von Gunten, 2000). HANs and i-THMs are two unregulated classes of semi-volatile DBPs also present in disinfected waters alongside other unregulated DBPs including halonitromethanes (HNMs), haloaldehydes (HAs) and haloketones (HKs) (Krasner et al., 2006). These semi-volatile DBPs are of interest because of their toxicity. HANs have been reported to be genotoxic and potentially carcinogenic for human health and HKs exerted carcinogenic or mutagenic effects in mice (Bull and Robinson, 1986; Daniel et al., 1986). Plewa et al. (2004) found HNMs to be toxic in chinese hamster ovary cells (CHO) and Richardson (2003) suggested than i-THMs could be more toxic than their brominated and chlorinated analogues. Despite their potential health effects, there is no UK or US regulatory limit for these compounds, but

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the WHO has suggested guideline values of 20 µg/L for DCAN, 70 µg/L for DBAN and 10 µg/L for TCA (WHO, 2006).

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

To have a better understanding of HAAs, THMs and semi-volatile DBPs in treated waters, their formation was evaluated under controlled conditions. Here 11 water treatment works selected from across England and Wales have been surveyed to allow us to determine the potential for formation, relative distribution and speciation of DBPs as well as identify any relationships between water sources. The DBPs selected include THM_4 (trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM)), HAA_9 (MCAA, MBAA, DCAA, TCAA, bromochloroacetic acid (BCAA), DBAA, bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromomethane (TBAA))

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plus four HANs (DCAN, trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN) and DBAN), two HKs (1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP)), two HAs (dichloroacetaldehyde (DCA) and TCA), two HNMs (trichlornitromethane (TCNM) and dibromonitromethane (DBNM)) and two i-THMs (dichloroiodomethane (DCIM) and bromochloroiodomethane (BCIM)). This is the first study that has reported the potential for formation of HAAs, THMs and a range of semi-volatile DBPs in drinking water in England and Wales. It is also the first European study to directly assess what impact the switch from chlorine to monochloramine would have on the concentrations of the DBPs found.

Materials and methods

Water samples

Treated water samples were collected in July 2008 from 11 water treatment works, spread geographically across England and Wales (Table 1). Samples were collected prior to disinfection in polyethylene or glass 1L bottles and shipped to Cranfield laboratory. These were then analysed for pH, non-purgeable organic matter (NPOC) using a TOC 5000 Analyser (Shimadzu, Milton Keynes, UK), ultraviolet (UV) absorbance at 254 nm, and specific ultraviolet absorbance (SUVA), which was calculated as the ratio of UV absorbance at 254 nm (m^{-1}) to NPOC (mg C L^{-1}). NPOC was used rather than DOC/TOC as the level of inorganic carbon in some samples was too high to enable accurate DOC/TOC measurement. Bromide and iodine were measured using inductively coupled plasma/mass spectrometry (ICP/MS) (Elan 9000,

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Perkin Elmer, UK). Total bromine and iodine measured were assumed to be primarily bromide and iodide.

Sample preparation

Chlorine and monochloramine solutions were prepared following the 4500-Cl B. Iodometric method I and 4500-Cl F. DPD Ferrous Titrimetric Method respectively (APHA, 1992). For the chlorinated samples, a 100 mL bottle was partly filled with the water sample, the buffer at pH 7.2 and the chlorine solution (chlorine:NPOC ratio was 3:1 on a weight basis). The bottle was filled completely and capped headspace free with a PTFE-lined cap. Samples were incubated for 24 hours at 20°C in the dark. For the monochloraminated samples, a chlorine to nitrogen mass ratio of 3:1 was used in all samples and addition of monochloramine was based on the NPOC level, with combined chlorine:NPOC ratio of 3:1 by weight. The procedure of monochloraminated samples was the same as that for chlorinated samples.

Ammonium chloride at a concentration of 100 mg L^{-1} was used to quench chlorine and monochloramine residual while not degrading HAAs, in particular HAA_3 (BDCAA, DBCAA and TBAA) (Singer et al., 2002). Ascorbic acid at a concentration of 35 mg L^{-1} was used to quench chlorine and monochloramine residual in THM and semi-volatile DBP samples. The choice is based on the fact that ascorbic acid has been shown not to degrade any of these 16 DBPs (Chinn et al., 2007).

DBP analytical methods

HAA_9 were extracted with a modified version of the US EPA Method 552.2 reported by Tung et al. (2006). The HAAs were converted to their methyl esters and quantified using gas chromatography coupled with an electron capture detector (GC/ECD)

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(Agilent 6890). THM_4, four HANs, two HKs, two HAs, two HNMs and two i-THMs were extracted with an adapted method from Krasner et al. (2001). Standards for THM_4, for halogenated volatiles as a mixture of DBPs (DCAN, TCAN, BCAN, DBAN, 1,1-DCP, 1,1,1-TCP and TCNM) and for TCA were available from Sigma-Aldrich Ltd (UK). DCA standard was provided by TCI Europe (Belgium); DBNM, DCIM and BCIM were obtained from Helix Biotech (Canada). A 30 mL sample was transferred to a 60 ml glass vial, then adjusted to a pH of 3.5 or less and extracted with 3 mL of MtBE containing an internal standard. The solvent phase containing the DBPs was separated from the aqueous phase by addition of 10 g of sodium sulphate and 1 g copper sulphate. Then the sample was shaken manually for 3 to 5 minutes. Once settled the top layer was finally transferred to an autosampler vial and analysed with GC/ECD (Agilent 6890). The instrument conditions were as follows. A volume of 1 µL was injected splitless with the detector set at 200°C. Separation was performed by a ZB-1ms column (30 m × 0.25 mm × 0.25 µm) with a helium carrier gas at a column flow rate of 1.0 mL/min. The initial oven temperature was 35°C and held for 22 minutes followed by a 10°C per minute temperature ramp to 145°C and held for 2 minutes and a final ramp of 20°C per minute ramp to 225°C and held for 10 minutes. The total run time was 49 minutes. The detector temperature was 290°C and the data were collected with a rate of 20 Hz. Quality assurance undertaken showed good reproducibility of the method and limits of detection were typically in the low µg L^{-1} range (Table 2).

Results and discussion

Water characterisation

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Samples of treated waters collected from drinking water treatment works across England and Wales were analysed for pH, NPOC, UV, bromine and iodine. These results are presented below along with calculated SUVA values (Table 1). The average NPOC concentration was 1.6 mg L^{-1} with the highest value (3.7 mg L^{-1}) found in LR and the lowest concentration (0.2 mg L^{-1}) in B1. The NPOC concentration of the lowland rivers (mean of 1.7 mg L^{-1}) was similar to that measured in the upland reservoirs (mean of 1.5 mg L^{-1}). SUVA values calculated here ranged from 1.5 m^{-1} L mg^{-1} C (B1) to 5.4 m^{-1} L mg^{-1} C (UR3). L1 and UR3, with low NPOC values (1.2 and 1.1 mg L^{-1} respectively), had high SUVA values of 4.6 and 5.4 m^{-1} L mg^{-1} C respectively, which indicate that the NOM was hydrophobic in character. No specific trends were observed between the water treatment processes used and the treated water SUVA values. The two waters with the highest SUVA (L1 and UR3) were treated with direct filtration, not coagulation which is more effective towards removal of hydrophobic material (Sharp et al., 2006).

The level of bromine, which we have assumed here to be mainly bromide, ranged from 14 to 310 µg L^{-1} (Table 1), with an average concentration of 105 µg L^{-1}. This is in agreement with the concentrations of bromide in natural waters reported by Amy et al. (1994) ranging from 30 to 200 µg L^{-1}, with an average of 100 µg L^{-1}. The highest concentrations were found in B1, LR, BR2 and BR3 and it is expected here that these waters with levels of bromide > 100 µg L^{-1} would form primarily brominated DBPs (Singer et al., 2002).

The level of iodine found during this survey varied between 0.9 and 16.7 µg L^{-1} (Table 1) and is in line with the findings of Fuge et al. (1986) who reported total iodine in water sources ranging between 0.5 and 20 µg L^{-1}. Interestingly the ratio of bromine to

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iodine here varied considerably between 1 and 22%, which indicates no specific trend between the level of bromine and iodine in the water sources.

DBP levels from different water sources

HAAs

The concentrations of nine HAAs from the 11 treated waters were quantified after exposure to chlorine and monochloramine (Figure 1). In Figure 1, chlorine data are represented as the treatment work reference only (e.g. B1) and the monochloramine data are shown as NH_2Cl-work reference (e.g. NH_2Cl-B1). It is clear that using monochloramine produced significantly less HAAs (average reduction of 77%) when compared to chlorine. These findings compare well with previous studies that have looked at HAA formation when using preformed monochloramine, typically a 90 to 95% reduction was observed (Cowman and Singer, 1996; Guay et al., 2005).

When chlorine was used as the disinfectant (Figure 1), considerable variation was observed between the individual waters with HAA levels ranging from 5.0 to 69 μg L^{-1}, with an average value of 37 μg L^{-1}. This is the first HAAFP data set published that we are aware of for England and Wales, although, Malliarou et al. (2005), earlier reported finished waters from three regions in England and Wales water and found means of 35, 52 and 95 μg L^{-1}.

Across the chlorinated water samples, the major species formed were TCAA (ranging from 1.0 to 40 μg L^{-1}) and DCAA (ranging from 2.5 to 22 μg L^{-1}). Sérodes et al. (2003) also found TCAA and DCAA to be the major species formed in treated waters from Quebec exposed to FP tests using chlorine. On a mass basis, DCAA and TCAA were followed here by BDCAA, BCAA, MCAA and DBCAA. The brominated HAAs

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MBAA, DBAA and TBAA were found at the lowest concentration and of these TBAA was not always detected.

The ratio of TCAA:DCAA varied across the chlorinated samples, with TCAA being predominant in six of the treated waters (B2, L2, UR1, UR2, UR3 and BR1), and DCAA for the remaining waters (B1, L1, LR, BR2 and BR3). Similar variations were also observed by Sérodes et al. (2003) and the excess chlorine used during FP tests as well as the bromine concentration is believed to be the cause. When the bromine concentration was ≤ 75 µg L^{-1}, TCAA was predominantly formed whilst when a high concentration of bromine (> 100 µg L^{-1}) (water samples B1, LR, BR2 and BR3) and an excess of chlorine were present, it is believed that bromide reacted to form hypobromous acid ($HOBr/OBr^-$), which is known to react with NOM faster than aqueous chlorine (Westerhoff et al., 2004). Consequently, the NaOCl to the NPOC ratio (NaOCl:NPOC), on a mass basis, decreased as the bromine increased. Miller and Uden (1983) amongst others found that at lower NaOCl:NPOC, the relative amount of DCAA formed was higher than that of TCAA, which was observed here. For example BR1, with a bromine concentration of 14 µg L^{-1}, formed 22 µg L^{-1} of DCAA and 40 µg L^{-1} of TCAA, whereas LR, with a bromine concentration of 209 µg L^{-1} formed 16 µg L^{-1} of DCAA and 12 µg L^{-1} of TCAA.

When monochloramine was used as the disinfectant the highest concentration of HAAs formed was 14 µg L^{-1} (L2, LR and BR1) and the average concentration 8.2 µg L^{-1} (Figure 1). DXAAs, and in particular DCAA, were the predominant HAAs formed, comprising at least 60% of the total HAA formation. This is expected as Karanfil et al. (2008) and Cowman and Singer (1996) both reported DXAA to be the main HAA species when using monochloramine and, in their studies, constituted 80 and 65%

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274 respectively of the total HAA formed. Monohalogenated HAAs (MXAA) were always
275 the minor HAAs formed and did not contribute more than 20%.

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

292 ***Bromine incorporation***

293 To assess the extent of bromine substitution in HAA when using chlorine and
294 monochloramine, the bromine incorporation factor (BIF) was calculated (Symons et al.,
295 1993):

296 $$BIF = \frac{HAABr_9\,(\mu mol\,L^{-1})}{HAA_9\,(\mu mol\,L^{-1})}, \qquad \text{Equation 1}$$

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where $HAABr_9$ is the sum of the molar concentrations of bromine incorporated in the nine HAA species and HAA_9 represents the sum of molar concentrations of all nine HAAs. The value BIF can range from zero to three. Calculated BIF values were plotted against the bromine concentration (Figure 2) and it was found that the correlation between BIF and bromine was better in water exposed to monochloramine ($R^2 = 0.72$) than to chlorine ($R^2 = 0.39$).

Overall the results show that BIF increased with increasing bromine concentrations, leading to more brominated HAAs. Also, BIF is higher in chlorinated waters than in monochloraminated waters. Chlorine is a more powerful oxidant and its reaction with bromine to form HOBr and then the formation of brominated HAAs will be faster and more predominant than with monochloramine (Deborde and Von Gunten, 2008).

THMs and i-THMs

As with the HAAs, shifting from chlorine to monochloramine produced significantly less THMs and the average reduction was 92% (Figure 3). While using chlorine there was considerable variation in THM levels across the 11 waters with concentrations ranging from 2.6 to 66 μg L^{-1}. The average concentration was 30 μg L^{-1}, which is similar to the value observed for the HAAs (average of 37 μg L^{-1}). The lowest concentration of THMs was found in L1 and the highest in LR, followed by L2. These results are similar to those for the HAAs, and specifically, the concentration of TCM was similar to that of TCAA in many samples, indicating possible common precursors. For example, in B2, TCM was 13 μg L^{-1} and TCAA was 11 μg L^{-1}, in UR1, both TCM and TCAA were at concentrations of 25 μg L^{-1} and in BR1, TCM was 35 μg L^{-1} and TCAA was 40 μg L^{-1}. It was observed that L1 had a lower concentration of THMs than L2 (2.6 and 47 μg L^{-1} respectively), both waters having the same NPOC values, but L1 having a greater SUVA value than L2, which indicates that neither NPOC, nor SUVA

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were effective surrogates for these two treated waters. In all the chlorinated waters with bromine < 50 μg L^{-1}, TCM was found to be the major THM species, whereas in those waters with bromine ≥ 75 μg L^{-1} brominated THMs became the major group.

When using monochloramine the concentrations of THMs were mostly below 1 μg L^{-1}, aside from B1, LR and BR2. Interestingly, BR2, which had the highest concentration of bromine (310 μg L^{-1}) could form brominated THMs (13 μg L^{-1}) even when using monochloramine as a disinfectant.

The concentrations of two i-THMs were also evaluated (Figure 4). The maximum concentration found here was 0.73 μg L^{-1} and most concentrations were below the MRL of 0.58 μg L^{-1}. Cancho et al. (2000) reported average levels lower than 1 μg L^{-1} for three species (DCIM, BCIM and DBIM) in sand filters and ozonated waters, and Krasner et al., (2006) reported a maximum of 19 μg L^{-1} for six i-THMs with DCIM and BCIM being the prevalent species. Overall the concentration of i-THMs formed was low when compared to THMs (Figure 4), with the ratio of the i-THMs to THMs being 1% on an average basis and 0.4% on a median basis. Krasner et al. (2006) reported a median ratio of 2% for six i-THMs and it known that chlorine can oxidise iodide through to iodate (IO_3^-) and, hence, minimises any potential for i-THM formation (Bichsel and Von Gunten, 1999). In the formation potential tests reported here chlorine is largely in excess and hence we would expect the formation of IO_3^- which is the likely reason for the low level of i-THMs and the lack of any correlation between the i-THMs and the iodine level in the water sources.

The formation of i-THMs is favoured by monochloramine because monochloramine, unlike chlorine, is unable to oxidise hypoiodus acid (HOI) to IO_3^- meaning that HOI has a longer lifetime with monochloramine and can react with NOM to form i-THMs (Bichsel and Von Gunten, 1999). Here, it was found that levels of i-THMs after

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monochloramine were between not detected to 0.89 μg L^{-1} (Figure 4), with five water samples (B1, B2, L1, L2 and BR2) having greater concentrations of i-THMs than after exposure to chlorine, whereas the contrary was observed in LR, UR1, UR2, UR3 and BR3.

HANs

When using chlorine, HANs were detected in all waters and their concentrations were typically an order of magnitude lower than the concentrations of THMs and HAAs (Figure 5). Total HAN concentrations ranged between 0.023 and 5.5 μg L^{-1}, which is in line with the findings of Krasner et al. (2007), who reported levels of dihalogenated HANs between approximately 0.80 μg L^{-1} and 6.2 μg L^{-1} when using FP tests. DCAN was the major HAN formed and contributed up to 56% of the total HAN, followed by BCAN (27%), DBAN (16%) and TCAN (2%). Dihalogenated HANs are reported to be more stable than the trihalogenated HANs by a number of authors (Peters et al., 1990; Singer et al., 1995). In addition, TCAN can undergo base-catalysed hydrolysis at pH higher than 5.5 (here, the pH was 7.2) which is likely to explain why it was rarely detected in this study (Croué and Reckhow, 1989).

DCAN was the most abundant species found in chlorinated waters containing levels of bromine < 50 μg L^{-1}. In the waters with bromine ≥ 75 μg L^{-1} the brominated HANs (BCAN and DBAN) were dominant (67% total HAN). Peters et al. (1990) reported a similar value with the brominated dihalogenated HANs accounting for 60% of the total HAN in Dutch surface waters with bromide concentrations ≥ 500 μg L^{-1}. Here the lowland waters L1, BR2 and BR3 produced more HANs which is expected as these sources are more likely to contain dissolved organic nitrogen, the main precursor for HANs (Oliver et al., 1983). The speciation observed was again dependent on the presence of bromine. For example BR2, which contains 310 μg L^{-1} of bromine, formed

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372 mainly BCAN and DBAN (0.31 and 0.39 μg L^{-1} respectively), whereas UR2 with a
373 bromine concentration of 18 μg L^{-1} formed 0.013 and 0.014 μg L^{-1} for both BCAN and
374 DBAN, but 0.26 μg L^{-1} of DCAN.

375 Changing from chlorine to monochloramine decreased the concentration of HANs by
376 81% (Figure 5). Hua and Reckhow (2007) also found that concentrations of HAN were
377 reduced by between 93% and 100% when using monochloramine and little
378 dihalogenated HANs (<1 μg L^{-1}) were formed.

379

380 ***HKs, HAs and HNMs***

381 The concentrations of the two HKs formed following exposure to chlorine and
382 monochloramine are presented (Figure 6). HKs were detected in all the treated waters
383 exposed to chlorine (Figure 6), with concentrations ranging from 0.37 to 3.9 μg L^{-1},
384 with a mean value of 1.8 μg L^{-1}. The highest concentration was observed in BR1,
385 whereas the lowest concentration was observed in L1 and B1. 1,1,1-TCP was the
386 major HK formed in B2, L2, LR, UR1, UR2, UR3, BR1, BR2 and BR3. The greater
387 formation of 1,1,1-TCP in the samples is believed to be the result of the excess chlorine
388 used in FP tests, involving the oxidation of 1,1-DCP to 1,1,1-TCP (Gurol *et al.*, 1983).

389 The use of monochloramine resulted on average in a decrease of 70% in the total HK
390 compared to the use of chlorine (Figure 6). No 1,1,1-TCP was detected which, given
391 that monochloramine does not provide enough free chlorine to push further substitution
392 into 1,1-DCP, was expected (Yang et al. (2007)

393 HAs were present in all samples after 24 hours contact time with chlorine (Figure 7).
394 The minimum value was 0.92 μg L^{-1} for L1 and the maximum value was 9.5 μg L^{-1} for
395 BR1. The average of HAs formed was 4.4 μg L^{-1} and this group of DBPs represented

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396 the third major class of halogenated DBPs formed (on a weight basis) after HAAs and
397 THMs. The major HA detected was TCA (also called chloral hydrate) and Williams et
398 al. (1997) also found TCA to be the most prevalent DBP after HAAs and THMs.
399 Koudjonou et al. (2008) also reported TCA in drinking water made up 60% of the total
400 HA. Ozonation is known to increase the levels of DCA and TCA (Weinberg et al.,
401 1993) and here if we consider the two boreholes B1 and B2 they have different
402 concentrations of HKs, with B2, the pre-ozonated site, having a greater formation
403 potential for DCA (0.62 μg L^{-1}) and TCA (2.4 μg L^{-1}) than B1 (0.31 and 0.61 μg L^{-1}
404 respectively), which has no ozone. The use of monochloramine resulted on average in
405 a 90% decrease in the total HA concentration (Figure 7).

406 The total concentration of HNMs measured after exposure to chlorine ranged from not
407 detected to 3.4 μg L^{-1} (Figure 8). The predominant HNM was TCNM and the
408 concentrations are in agreement with Krasner et al. (2001) who reported TCNM
409 concentrations of up to 2.0 μg L^{-1}. DBNM was detected here in B1, B2, L2, LR, BR2
410 and BR3, with the highest concentration found in BR2. Although other researchers have
411 shown that pre-ozonation can increase the formation of TCNM (Hoigné and Bader,
412 1988) or other HNMs (Plewa et al., 2004), it was not possible to see this trend here. The
413 highest concentration of HNMs was observed in BR1, a lowland river, followed by
414 UR1, which is an upland reservoir. On average the concentration of HNM was reduced
415 by 81% when using monochloramine and agrees with the recent findings of Hua and
416 Reckhow (2007) who showed that when using monochloramine only traces
417 concentrations of TCNM and those of Zhang et al. (2000) who reported a decrease of
418 58% with monochloramine in comparison to chlorine.

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Relative toxicity of DBPs measured

Although, HAAs and THMs were more significant in regards to the mass concentration than the semi-volatile DBPs, it should be noted that the toxicity of some of the semi-volatile DBPs is much higher than the toxicity for HAAs and THMs. As shown in Figure 9, Plewa et al. (2008) reported that the genotoxicity and the cytotoxicity were much higher for the nitrogen-containing compounds HANs and HNMs than the THMs and HAAs. Furthermore, the same authors reported that the iodo- and bromo-DBPs were more cytotoxic and genotoxic than their chlorinated counterparts, and this is because iodine and bromine are better leaving groups than chlorine due to their greater polarisable bondings (Woo et al., 2002). Therefore, here, despite their lower concentrations, some of the semi-volatile DBPs are more significant than HAAs and THMs from a health standpoint.

Relationships between HAAs, THMs and other DBPs

Here the correlation between HAAs and THMs was investigated (Figure 10) and it was found that for the waters evaluated that THMs were generally a good surrogate for HAAs when chlorine was used (coefficient of correlation $R^2 = 0.82$). The slope of this correlation was 1.21, which suggests that there is slightly more than one microgram of HAA formed for one microgram of THM. No correlation could be found between THM and HAAs when using monochloramine. Malliarou et al. (2005) also reported a good relationship between THM and HAAs in final waters from two geographically different regions in England and Wales ($R^2 = 0.82$ and 0.90), whereas they found a poor correlation in the waters of their third region investigated and suggested that total THM could not be assumed to be a good indicator for HAA levels. Moderate relationships

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were also found between the total THM and the sum of the semi-volatile DBPs (HAN, HA, HK, i-THM and HNM) measured after exposure to chlorine (Figure 10). The R^2 obtained for the collated semi-volatile DBPs was 0.68, which is in line with a previous correlation (R^2 = 0.76) found between total THM and non-THM DBPs in drinking waters (Krasner et al., 1989). This correlation suggests that the control of THM precursors is closely linked to the control of other DBP precursors. As explained by Krasner et al. (1989) this trend is valid for the sum of the measured halogenated DBPs but it does not give similar trends for individual compounds; e.g. comparing total THMs to HNMs yields an R^2 of only 0.08. In terms of regulation, it is interesting to note that the regulatory limit of 100 μg L^{-1} for the THM_4 would fail a regulation of 80 μg L^{-1} for the nine HAAs, currently under consideration by the European Union (Cortvriend, 2008). Indeed from the correlation found here, if 100 μg L^{-1} of THM_4 would be formed, it would be expected to form 121 μg L^{-1} of HAA_9. In the specific waters investigated here, to achieve a concentration of 80 μg L^{-1} for HAA_9, THM_4 should be no higher that 65 μg L^{-1}.

Relationships between NPOC, UV and SUVA with DBPs

Relationships between NPOC, UV and SUVA with HAAs, THMs and the semi-volatile DBPs were investigated with chlorine FP test data. NPOC, UV and SUVA have been used previously as surrogates for measuring DBPs as they are easier, cheaper and faster to measure than DBPs (Goslan et al., 2002; Parsons et al., 2005; Ates et al., 2007). Firstly, HAAs, THMs and semi-volatile DBPs have been correlated against NPOC and correlation (R^2 values) between NPOC and HAAs, THMs and the semi-volatile DBPs (collated together) were moderate (0.51, 0.63 and 0.56 respectively). Although stronger correlations have been reported, such as White et al. (2003), who found an R^2

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of 0.86 and 0.87 for HAAs and THMs respectively to NPOC, it is likely that correlations observed in a single sample are better than correlations observed from a range of water sources. In terms of semi-volatile DBPs as separate species it was observed that NPOC correlated well with HANs (R^2 = 0.82) and moderately with HAs (R^2 = 0.52) (Table 3). However, no correlations were found between NPOC with i-THMs, HNMs and HKs. No correlations were found between either SUVA or UV_{254} and DBPs was also investigated (Table 3).

Conclusions

- The results have shown how all the waters have the potential to form significant levels of all the DBPs monitored for and that in general a decrease in concentration was been observed when shifting from chlorine to monochloramine, the one exception being 1,1-DCP.
- In general the concentrations of THMs correlated well with HAAs, and in particular the levels of TCM were similar to the levels of TCAA supporting the hypothesis that they share similar precursor material.
- The impact of bromide on the formation of DBPs is well documented in the literature and here the data reaffirmed that more bromide species are formed in high bromide-containing waters. For HAAs, brominated species are predominant when bromine was > 100 µg L^{-1}, whereas the brominated THMs dominated when bromine was ≥ 75 µg L^{-1}.
- The use of FP test was found here to be unsuitable for the quantification of i-THMs as the high chlorine levels are likely to limit formation.

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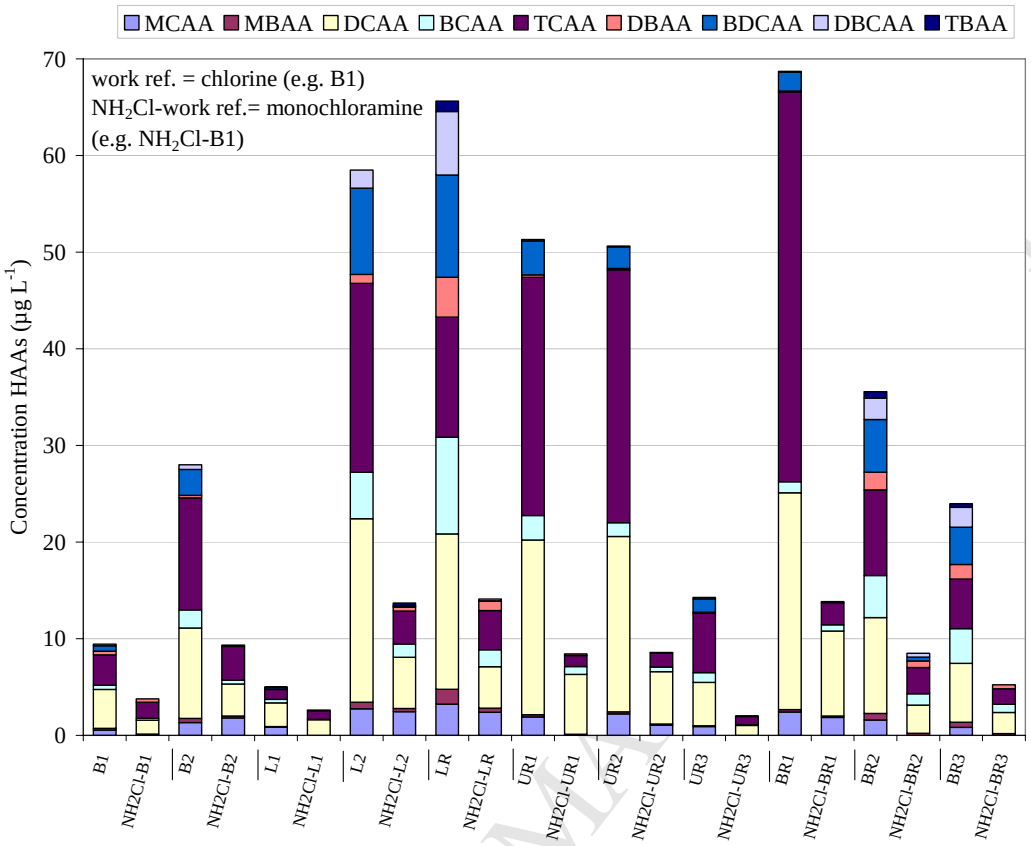


Figure 1. Distribution of HAAs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

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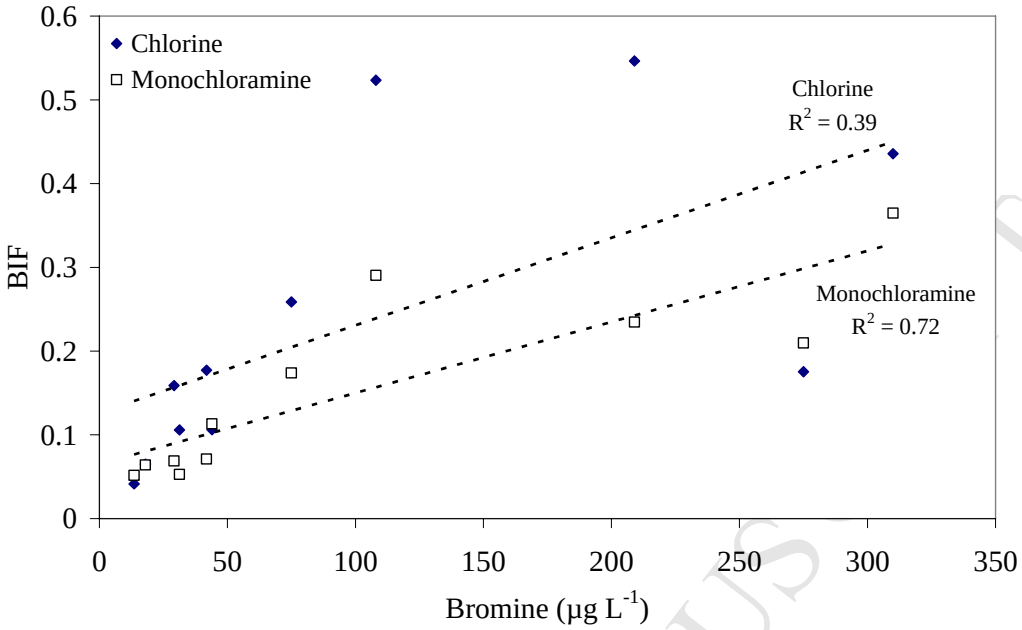


Figure 2. BIF in chlorinated and monochloraminated samples versus bromine concentration

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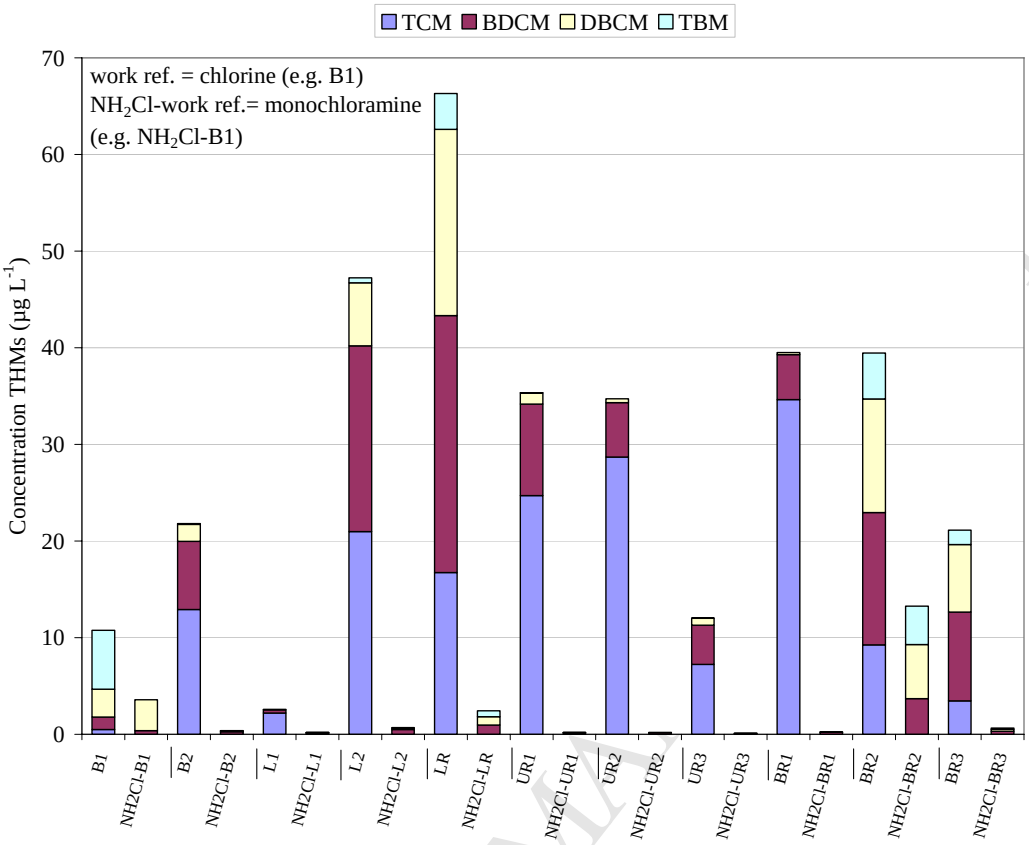


Figure 3. Distribution of THMs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

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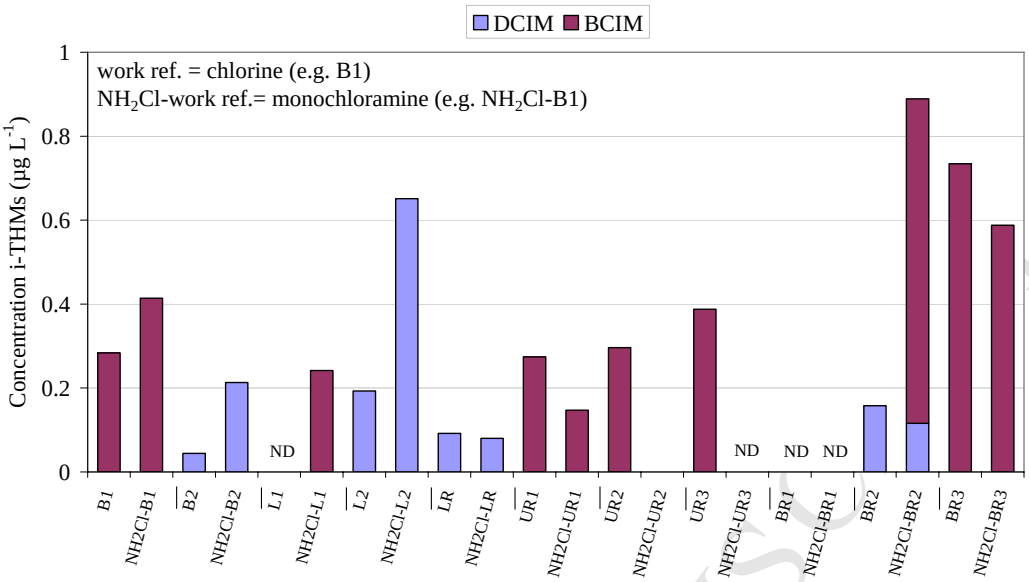


Figure 4. Distribution of i-THMs after 24 hours bench exposure to chlorine and monochloramine for 11 treated waters (ND – not detected)

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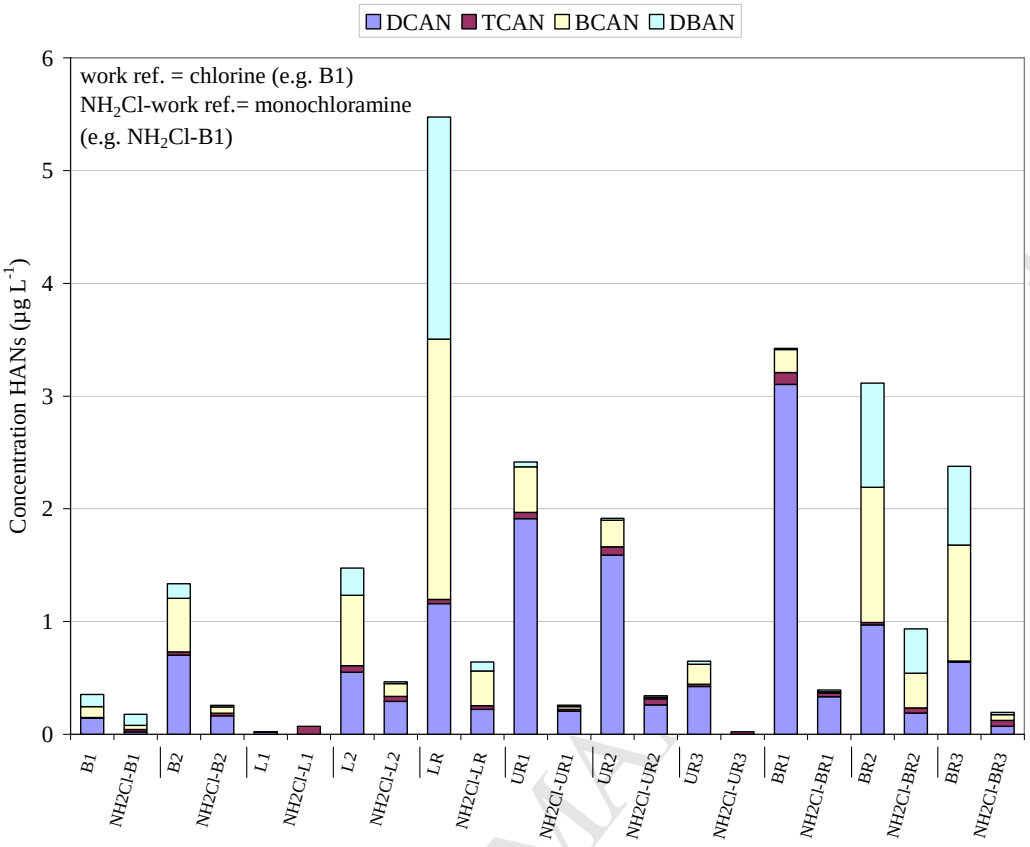


Figure 5. Distribution of HANs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

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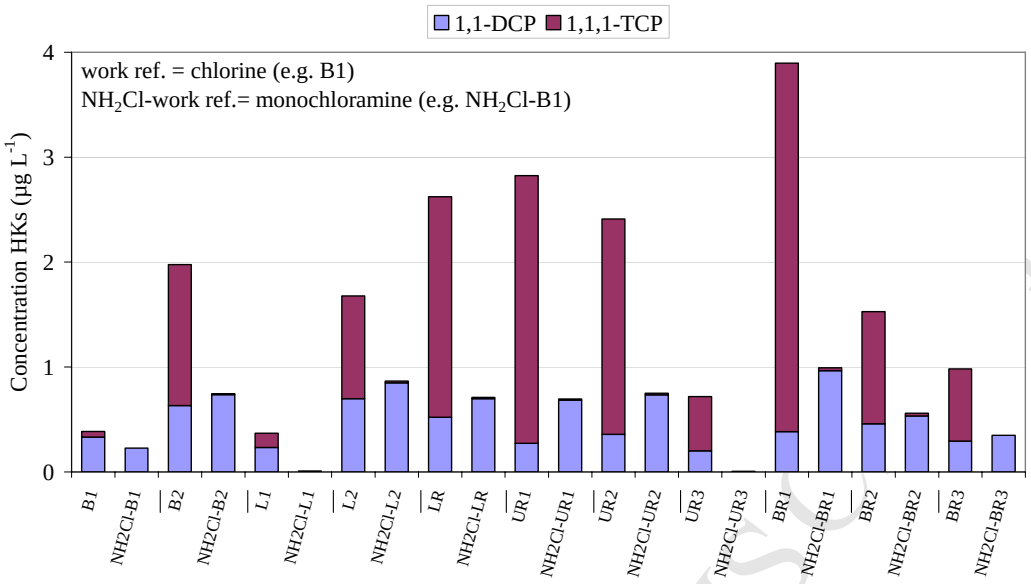


Figure 6. Distribution of HKs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

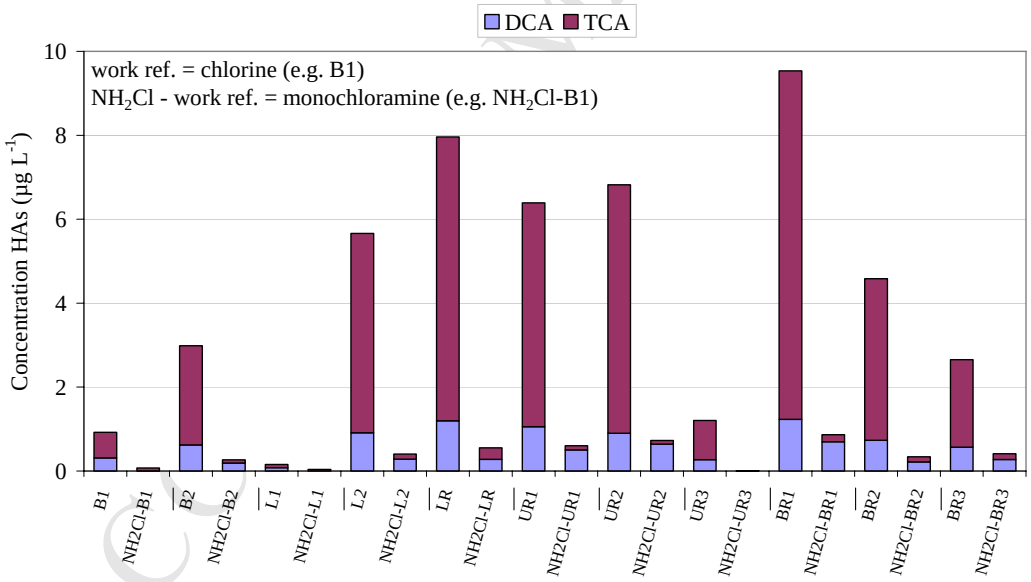


Figure 7. Distribution of HAs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

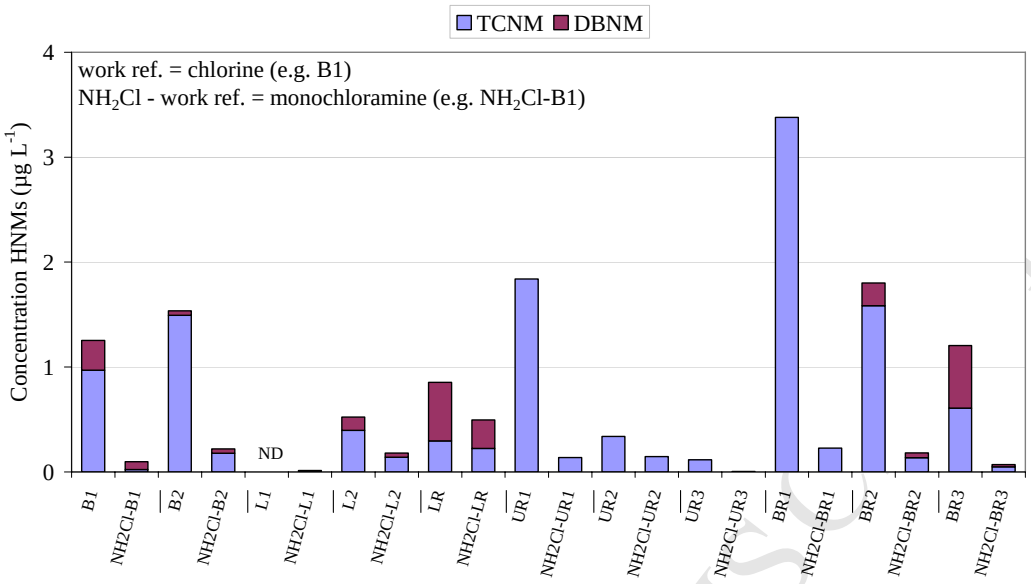


Figure 8. Distribution of HNMs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters (ND – not detected)

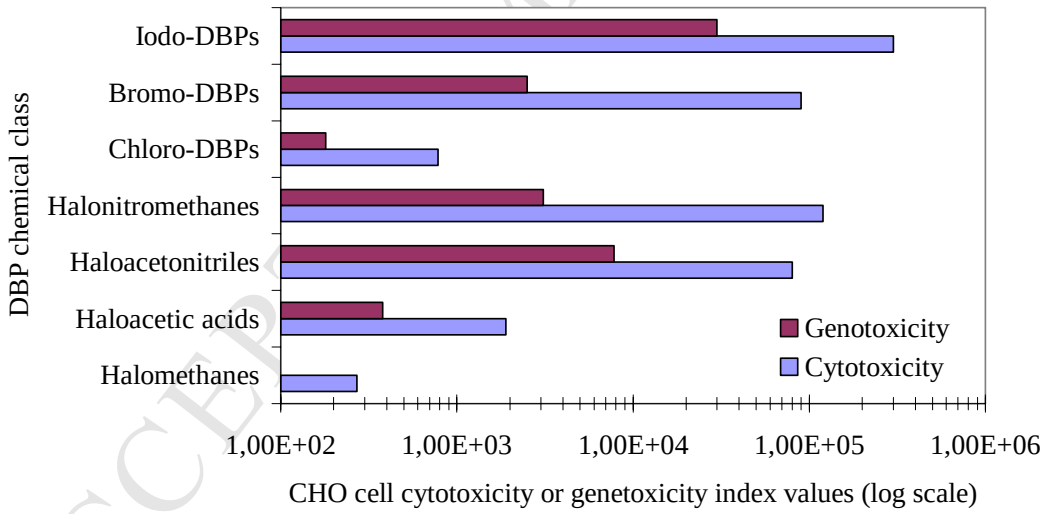


Figure 9. Cytotoxicity and genetoxicity indices for different classes of DBPs and for chloro-, bromo- and iodo-DBPs (Adapted from Plewa et al., 2008)

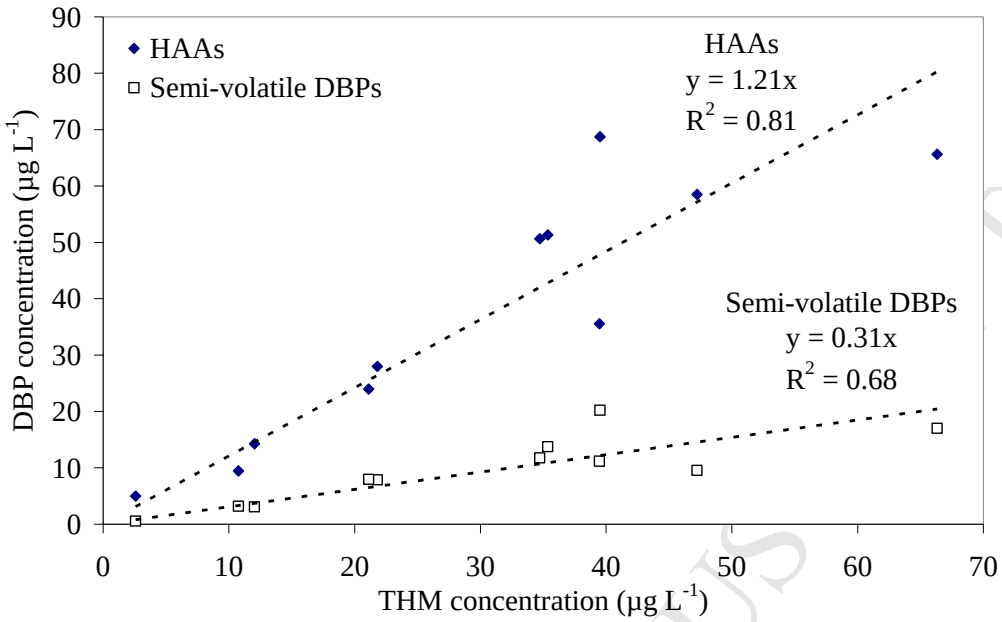


Figure 10. Correlation between THMs with HAAs and the semi-volatile DBPs (chlorine FP tests)

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Table 1. List of water treatment works, sources and water characteristics

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

ref. – reference

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Table 2. Method performance

Compound	Average tr[a] (min)	RSD[b] (%)	Detection Limit[c] (µg/L)	MRL[d] (µg/L)
TCM	7.72	0.058	0.088	0.264
DCA	7.95	0.052	0.124	0.371
TCAN	9.99	0.042	0.020	0.061
DCAN	11.17	0.060	0.019	0.057
BDCM	11.24	0.063	0.036	0.108
TCA	12.02	0.035	0.029	0.086
1,1-DCP	13.12	0.030	0.029	0.086
TCNM	18.53	0.059	0.039	0.117
BDCM	19.10	0.045	0.049	0.148
BCAN	20.01	0.042	0.023	0.070
DCIM	22.64	0.067	0.086	0.257
1,1,1-TCP	25.28	0.013	0.089	0.268
TBM	27.10	0.037	0.095	0.284
DBAN	27.71	0.009	0.014	0.041
BCIM	28.28	0.015	0.108	0.324
DBNM	28.81	0.012	0.059	0.178

[a] The average retention time corresponds to the average of seven injections; [b] Corresponds to the relative standard deviation and must be less than 15% according to US EPA Method 551.1 (1995a); [c] Fortified waters were extracted and analysed over 3 days for seven replicates; [d] Corresponds to the minimum reporting level and is the threshold expected for accurate quantification in an unknown sample. It has to be at least three times the limit of detection.

Table 3. Correlation between DBPs and water characteristics

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

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Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine

Bougeard, M. M.; Goslan, Emma H.; Jefferson, Bruce; Parsons, Simon A.

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