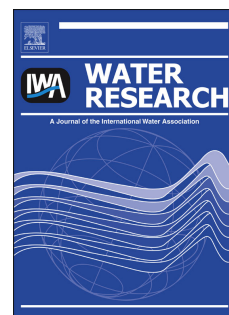


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Authors: Cynthia M.M. Bougeard, Emma H. Goslan, Bruce Jefferson, Simon A. Parsons



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

Cynthia M.M. Bougeard, Emma H. Goslan, Bruce Jefferson and Simon A. Parsons*

Centre for Water Science, Cranfield University, Bedfordshire, MK43 0AL, UK

* - corresponding author. Tel.: +44 1234 758311. Fax: +44 1234 751671. E-mail:

s.a.parsons@cranfield.ac.uk.

9 Abstract

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

22
 23 **Key words:** disinfection by-products, trihalomethanes, haloacetic acids,
 24 haloacetonitriles, monochloramination, semi-volatile DBPs

26 Abbreviations

27 1,1-DCP – 1,1- dichloropropanone
 28 1,1,1-TCP – 1,1,1- trichloropropanone
 29 BCAA – bromochloroacetic acid
 30 BCIM – bromochloroiodomethane
 31 BDCAA – bromodichloroacetic acid
 32 BDCM - bromodichloromethane

- 33 BIF – bromine incorporation factor
- 34 CHO – Chinese hamster ovary cells
- 35 DBAA – dibromoacetic acid
- 36 DBAN –dibromoacetonitrile
- 37 DBCAA – dibromochloroacetic acid
- 38 DBCM – dibromochloromethane
- 39 DBIM – dibromiodomethane
- 40 DBNM – dibromonitromethane
- 41 DBPs – disinfection by-products
- 42 DCA – dichloroacetaldehyde
- 43 DCAA – dichloroacetic acid
- 44 DCAN - dichloroacetonitrile
- 45 DCBM – dichlorobromomethane
- 46 DCIM – dichloriodomethane
- 47 DXAA – dihalogenated acetic acids
- 48 FP – formation potential
- 49 GC-ECD – gas chromatography electron capture detection
- 50 HAs - haloaldehydes
- 51 HAAs – haloacetic acids
- 52 HANs – haloacetonitriles
- 53 HKs – haloketones
- 54 HNMs – halonitromethanes
- 55 HOBr/OBr⁻ – hypobromous acid
- 56 HOI – hypoiodous acid
- 57 ICP/MS – inductively coupled plasma/mass spectrometry

- 58 IO_3^- - iodate
59 i-THMs – iodo THMs
60 MXAA – monohalogenated acetic acids
61 MtBE – methyl tert butyl ether
62 NaOCl – hypochlorous acid
63 NOM – natural organic matter
64 NPOC – non-purgeable organic carbon
65 SUVA – specific ultraviolet absorbance
66 TBAA – tribromoacetic acid
67 TBM – tribromomethane
68 TCA – trichloroacetaldehyde
69 TCAA – trichloroacetic acid
70 TCAN – trichloroacetonitrile
71 TCM – trichloromethane
72 TCNM – trichloronitromethane
73 TXAA – trihalogenated acetic acids
74 THMs – trihalomethanes
75 US EPA – United States Environmental Protection Agency
76 UV – ultraviolet absorbance

77

78 **Introduction**

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

83 sum of four THMs does not exceed $100 \mu\text{g L}^{-1}$ with a frequency of sampling dependent
84 on the population size. Haloacetic acids (HAAs) are often found to be as prevalent as
85 THMs but are currently not regulated in the UK. However, the European Union is
86 considering regulating the nine HAAs at $80 \mu\text{g L}^{-1}$ (Cortvriend, 2008) and as such there
87 is growing interest in the levels of these compounds found in UK drinking waters and
88 how best to control them. In order to comply with these proposed regulations, there
89 has been an increasing interest in using monochloramine as a secondary disinfectant
90 because of reduced DBP formation and its ability to provide residuals in water
91 distribution systems. Monochloramine is known to only form trace amounts of THMs
92 and HAAs, but the formation of dihalogenated HAAs (DXAAs), although generally
93 lower than with chlorine, can still reach significant levels depending on the dose,
94 chlorine to ammonia ratio, pH and other conditions (Diehl et al., 2000; Hua and
95 Reckhow, 2007). The use of monochloramine may also lead to an increase in other
96 DBPs such as haloacetonitriles (HANs) and iodo- THMs (i-THMs) (Krasner et al.,
97 1989; Bichsel and Von Gunten, 2000). HANs and i-THMs are two unregulated classes
98 of semi-volatile DBPs also present in disinfected waters alongside other unregulated
99 DBPs including halonitromethanes (HNMs), haloaldehydes (HAs) and haloketones
100 (HKs) (Krasner et al., 2006). These semi-volatile DBPs are of interest because of their
101 toxicity. HANs have been reported to be genotoxic and potentially carcinogenic for
102 human health and HKs exerted carcinogenic or mutagenic effects in mice (Bull and
103 Robinson, 1986; Daniel et al., 1986). Plewa et al. (2004) found HNMs to be toxic in
104 chinese hamster ovary cells (CHO) and Richardson (2003) suggested that i-THMs
105 could be more toxic than their brominated and chlorinated analogues. Despite their
106 potential health effects, there is no UK or US regulatory limit for these compounds, but

107 the WHO has suggested guideline values of 20 µg/L for DCAN, 70 µg/L for DBAN and
108 10 µg/L for TCA (WHO, 2006).

109 Past research has established that levels of HAAs and THMs in chlorinated waters vary
110 according to the levels of their precursors. High NOM concentrations have generally
111 been associated with high HAA and THM concentrations (Liang and Singer, 2003;
112 Sharp et al., 2006) and nitrogenous precursors from algae or effluent organic matter
113 (EfOM) have been related to nitrogenous DBPs, such as HANs (Oliver et al., 1983).
114 The presence of bromide in water will also affect the concentration of DBPs as will
115 other factors such as the disinfectant dose applied, the pH, the temperature of the water
116 samples and the reaction time of disinfectant in water (Singer et al., 2002). To better
117 control and understand the formation of DBPs in water samples, the use of formation
118 potential (FP) tests have been widely used (Zhang et al., 2000; Liang and Singer, 2003;
119 Ates et al., 2007; Krasner et al., 2007). FP tests are usually conducted at bench scale
120 with controlled pH, controlled temperature and relatively high chlorine concentration
121 dosed for a long contact time in order to maximise DBPs formation (Krasner et al.,
122 2007).

123 To have a better understanding of HAAs, THMs and semi-volatile DBPs in treated
124 waters, their formation was evaluated under controlled conditions. Here 11 water
125 treatment works selected from across England and Wales have been surveyed to allow
126 us to determine the potential for formation, relative distribution and speciation of DBPs
127 as well as identify any relationships between water sources. The DBPs selected include
128 THM₄ (trichloromethane (TCM), bromodichloromethane (BDCM),
129 dibromochloromethane (DBCM) and tribromomethane (TBM)), HAA₉ (MCAA,
130 MBAA, DCAA, TCAA, bromochloroacetic acid (BCAA), DBAA, bromodichloroacetic
131 acid (BDCAA), dibromochloroacetic acid (DBCBA), and tribromomethane (TBAA))

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 (trichloronitromethane (TCNM) and dibromonitromethane (DBNM)) and two i-THMs (dichloriodomethane (DCIM) and bromochloriodomethane (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.

141

142

143 **Materials and methods**

144 **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,

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

157 **Sample preparation**

158 Chlorine and monochloramine solutions were prepared following the 4500-Cl B.
159 Iodometric method I and 4500-Cl F. DPD Ferrous Titrimetric Method respectively
160 (APHA, 1992). For the chlorinated samples, a 100 mL bottle was partly filled with the
161 water sample, the buffer at pH 7.2 and the chlorine solution (chlorine:NPOC ratio was
162 3:1 on a weight basis). The bottle was filled completely and capped headspace free with
163 a PTFE-lined cap. Samples were incubated for 24 hours at 20°C in the dark. For the
164 monochloraminated samples, a chlorine to nitrogen mass ratio of 3:1 was used in all
165 samples and addition of monochloramine was based on the NPOC level, with combined
166 chlorine:NPOC ratio of 3:1 by weight. The procedure of monochloraminated samples
167 was the same as that for chlorinated samples.

168 Ammonium chloride at a concentration of 100 mg L⁻¹ was used to quench chlorine and
169 monochloramine residual while not degrading HAAs, in particular HAA₃ (BDCAA,
170 DBCAA and TBAA) (Singer et al., 2002). Ascorbic acid at a concentration of 35 mg L⁻¹
171 was used to quench chlorine and monochloramine residual in THM and semi-volatile
172 DBP samples. The choice is based on the fact that ascorbic acid has been shown not to
173 degrade any of these 16 DBPs (Chinn et al., 2007).

174

175 **DBP analytical methods**

176 HAA₉ were extracted with a modified version of the US EPA Method 552.2 reported by
177 Tung et al. (2006). The HAAs were converted to their methyl esters and quantified
178 using gas chromatography coupled with an electron capture detector (GC/ECD)

(Agilent 6890). THM₄, 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 THM₄, 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 μ L was injected splitless with the detector set at 200°C. Separation was performed by a ZB-1ms column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m) 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 μ g L⁻¹ range (Table 2).

Results and discussion

Water characterisation

202 Samples of treated waters collected from drinking water treatment works across
 203 England and Wales were analysed for pH, NPOC, UV, bromine and iodine. These
 204 results are presented below along with calculated SUVA values (Table 1). The average
 205 NPOC concentration was 1.6 mg L^{-1} with the highest value (3.7 mg L^{-1}) found in LR
 206 and the lowest concentration (0.2 mg L^{-1}) in B1. The NPOC concentration of the
 207 lowland rivers (mean of 1.7 mg L^{-1}) was similar to that measured in the upland
 208 reservoirs (mean of 1.5 mg L^{-1}). SUVA values calculated here ranged from $1.5 \text{ m}^{-1} \text{ L}$
 209 $\text{mg}^{-1} \text{ C}$ (B1) to $5.4 \text{ m}^{-1} \text{ L mg}^{-1} \text{ C}$ (UR3). L1 and UR3, with low NPOC values (1.2 and
 210 1.1 mg L^{-1} respectively), had high SUVA values of 4.6 and $5.4 \text{ m}^{-1} \text{ L mg}^{-1} \text{ C}$
 211 respectively, which indicate that the NOM was hydrophobic in character. No specific
 212 trends were observed between the water treatment processes used and the treated water
 213 SUVA values. The two waters with the highest SUVA (L1 and UR3) were treated with
 214 direct filtration, not coagulation which is more effective towards removal of
 215 hydrophobic material (Sharp et al., 2006).

216 The level of bromine, which we have assumed here to be mainly bromide, ranged from
 217 14 to $310 \text{ } \mu\text{g L}^{-1}$ (Table 1), with an average concentration of $105 \text{ } \mu\text{g L}^{-1}$. This is in
 218 agreement with the concentrations of bromide in natural waters reported by Amy et al.
 219 (1994) ranging from 30 to $200 \text{ } \mu\text{g L}^{-1}$, with an average of $100 \text{ } \mu\text{g L}^{-1}$. The highest
 220 concentrations were found in B1, LR, BR2 and BR3 and it is expected here that these
 221 waters with levels of bromide $> 100 \text{ } \mu\text{g L}^{-1}$ would form primarily brominated DBPs
 222 (Singer et al., 2002).

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

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

DBP levels from different water sources

HAA_s

The concentrations of nine HAA_s 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 NH₂Cl-work reference (e.g. NH₂Cl-B1). It is clear that using monochloramine produced significantly less HAA_s (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 HAA_s

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

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

268 When monochloramine was used as the disinfectant the highest concentration of HAAs
 269 formed was $14 \mu\text{g L}^{-1}$ (L2, LR and BR1) and the average concentration $8.2 \mu\text{g L}^{-1}$
 270 (Figure 1). DXAAs, and in particular DCAA, were the predominant HAAs formed,
 271 comprising at least 60% of the total HAA formation. This is expected as Karanfil et al.
 272 (2008) and Cowman and Singer (1996) both reported DXAA to be the main HAA
 273 species when using monochloramine and, in their studies, constituted 80 and 65%

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):

$$296 \quad \text{BIF} = \frac{\text{HAABr}_9 (\mu\text{mol L}^{-1})}{\text{HAA}_9 (\mu\text{mol L}^{-1})}, \quad \text{Equation 1}$$

where HAABr_9 is the sum of the molar concentrations of bromine incorporated in the nine HAA species and HAA_9 represents the sum of molar concentrations of all nine HAAs. The value BIF can range from zero to three. Calculated BIF values were plotted against the bromine concentration (Figure 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 $\mu\text{g L}^{-1}$. The average concentration was 30 $\mu\text{g L}^{-1}$, which is similar to the value observed for the HAAs (average of 37 $\mu\text{g L}^{-1}$). 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 $\mu\text{g L}^{-1}$ and TCAA was 11 $\mu\text{g L}^{-1}$, in UR1, both TCM and TCAA were at concentrations of 25 $\mu\text{g L}^{-1}$ and in BR1, TCM was 35 $\mu\text{g L}^{-1}$ and TCAA was 40 $\mu\text{g L}^{-1}$. It was observed that L1 had a lower concentration of THMs than L2 (2.6 and 47 $\mu\text{g L}^{-1}$ respectively), both waters having the same NPOC values, but L1 having a greater SUVA value than L2, which indicates that neither NPOC, nor SUVA

322 were effective surrogates for these two treated waters. In all the chlorinated waters
323 with bromine $< 50 \mu\text{g L}^{-1}$, TCM was found to be the major THM species, whereas in
324 those waters with bromine $\geq 75 \mu\text{g L}^{-1}$ brominated THMs became the major group.

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

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

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

monochloramine were between not detected to $0.89 \mu\text{g L}^{-1}$ (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 $5.5 \mu\text{g L}^{-1}$, which is in line with the findings of Krasner et al. (2007), who reported levels of dihalogenated HANs between approximately $0.80 \mu\text{g L}^{-1}$ and $6.2 \mu\text{g L}^{-1}$ 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 $< 50 \mu\text{g L}^{-1}$. In the waters with bromine $\geq 75 \mu\text{g L}^{-1}$ 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 $\geq 500 \mu\text{g L}^{-1}$. 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 $310 \mu\text{g L}^{-1}$ of bromine, formed

mainly BCAN and DBAN (0.31 and $0.39 \mu\text{g L}^{-1}$ respectively), whereas UR2 with a bromine concentration of $18 \mu\text{g L}^{-1}$ formed 0.013 and $0.014 \mu\text{g L}^{-1}$ for both BCAN and DBAN, but $0.26 \mu\text{g L}^{-1}$ of DCAN.

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

HKs, HAs and HNMs

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

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

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

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

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

421 **Relative toxicity of DBPs measured**

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

434 **Relationships between HAAs, THMs and other DBPs**

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

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 $100 \mu\text{g L}^{-1}$ for the THM_4 would fail a regulation of $80 \mu\text{g L}^{-1}$ for the nine HAAs, currently under consideration by the European Union (Cortvriend, 2008). Indeed from the correlation found here, if $100 \mu\text{g L}^{-1}$ of THM_4 would be formed, it would be expected to form $121 \mu\text{g L}^{-1}$ of HAA_9 . In the specific waters investigated here, to achieve a concentration of $80 \mu\text{g L}^{-1}$ for HAA_9 , THM_4 should be no higher than $65 \mu\text{g L}^{-1}$.

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

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 HAAs ($R^2 = 0.52$) (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 $> 100 \mu\text{g L}^{-1}$, whereas the brominated THMs dominated when bromine was $\geq 75 \mu\text{g L}^{-1}$.
- 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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501

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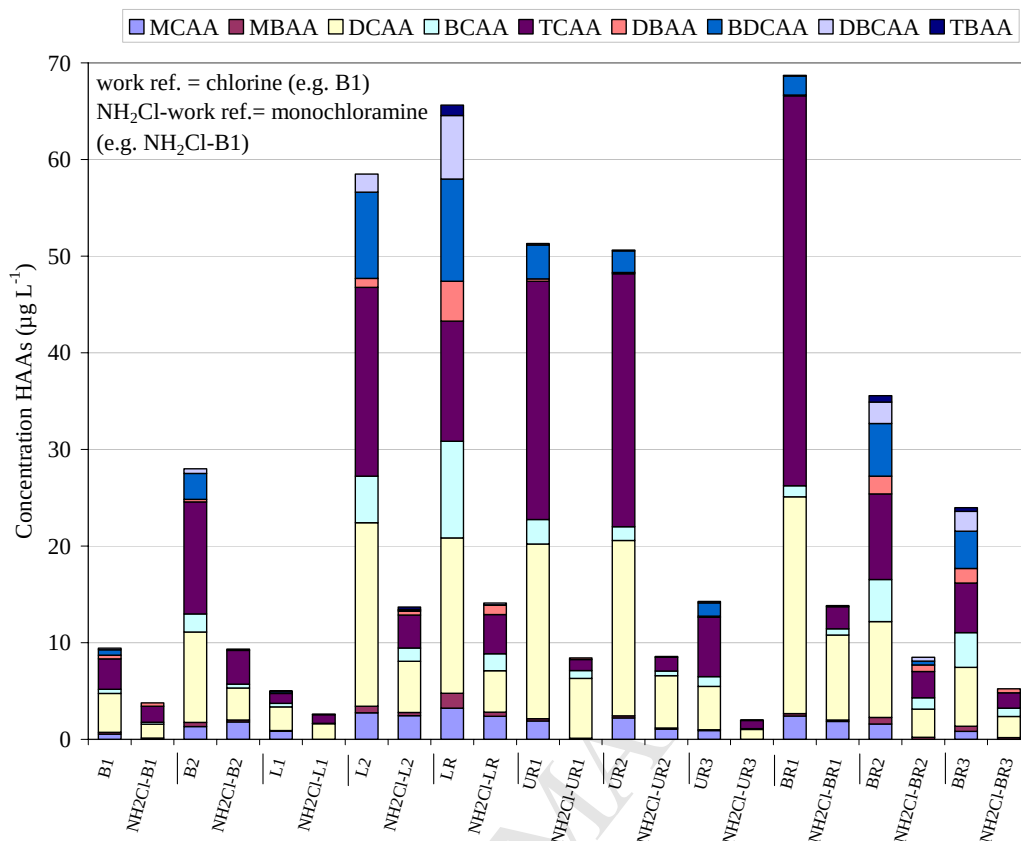


Figure 1. Distribution of HAAs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

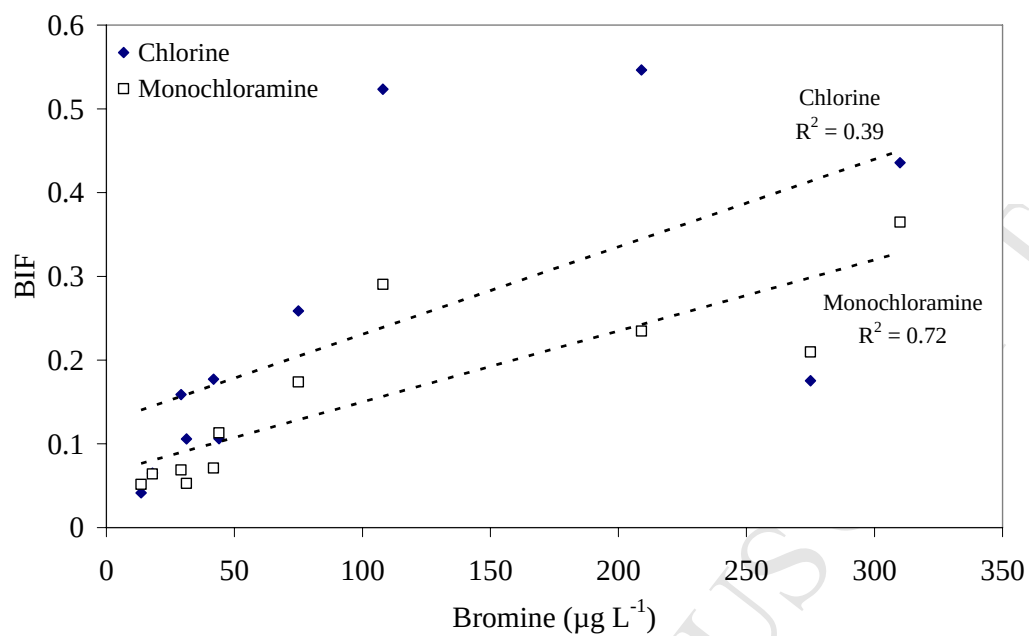


Figure 2. BIF in chlorinated and monochloraminated samples versus bromine concentration

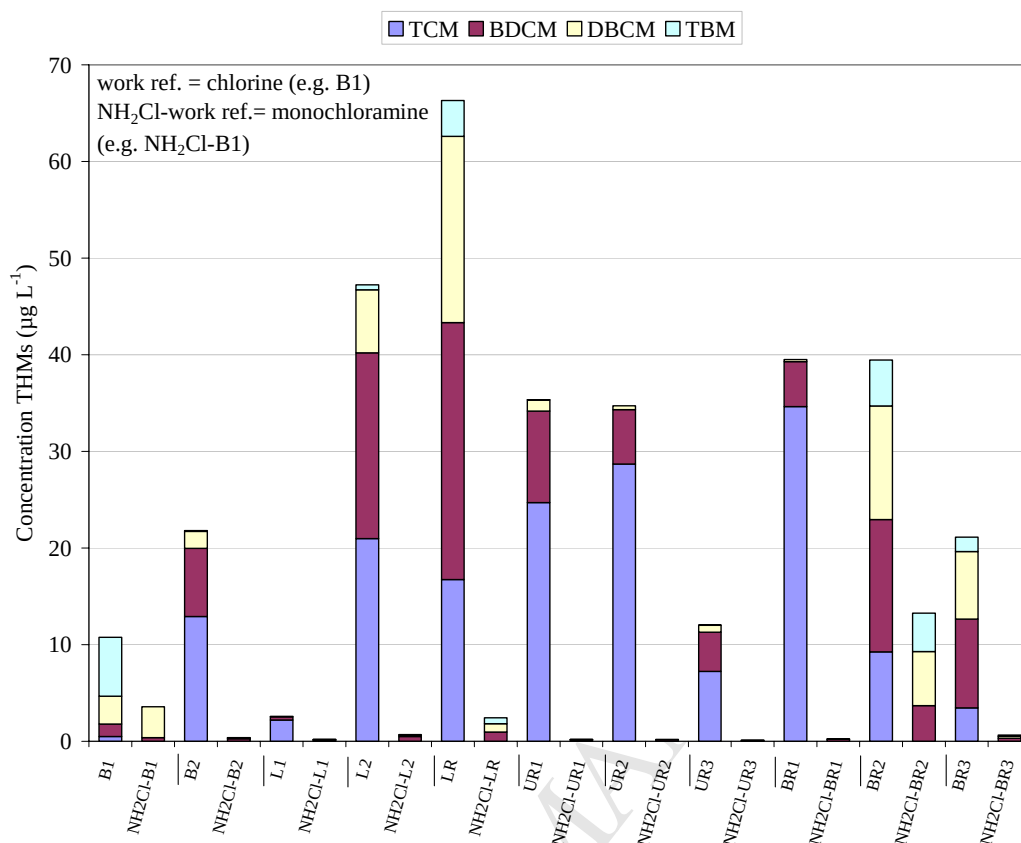


Figure 3. Distribution of THMs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

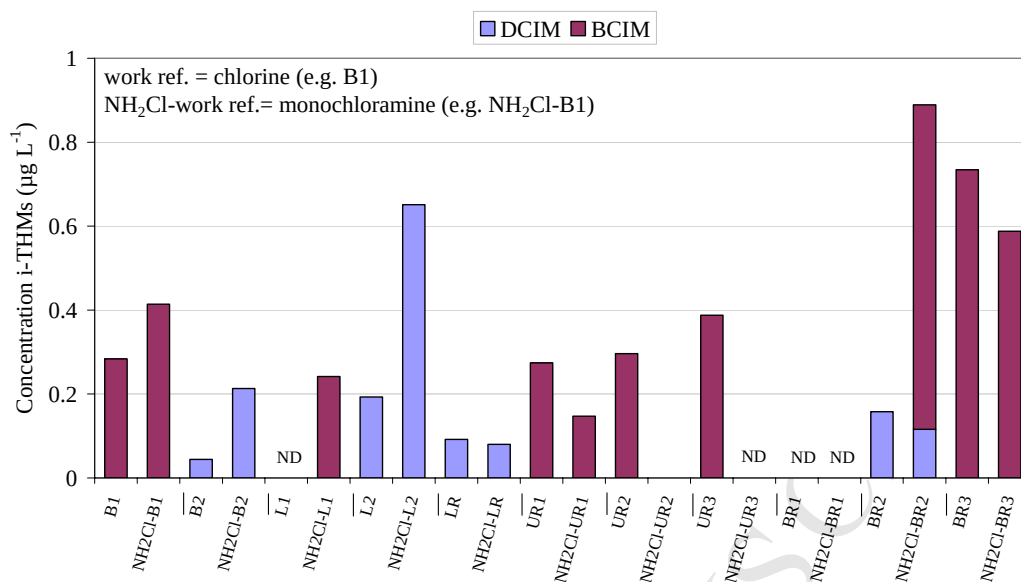


Figure 4. Distribution of i-THMs after 24 hours bench exposure to chlorine and monochloramine for 11 treated waters (ND – not detected)

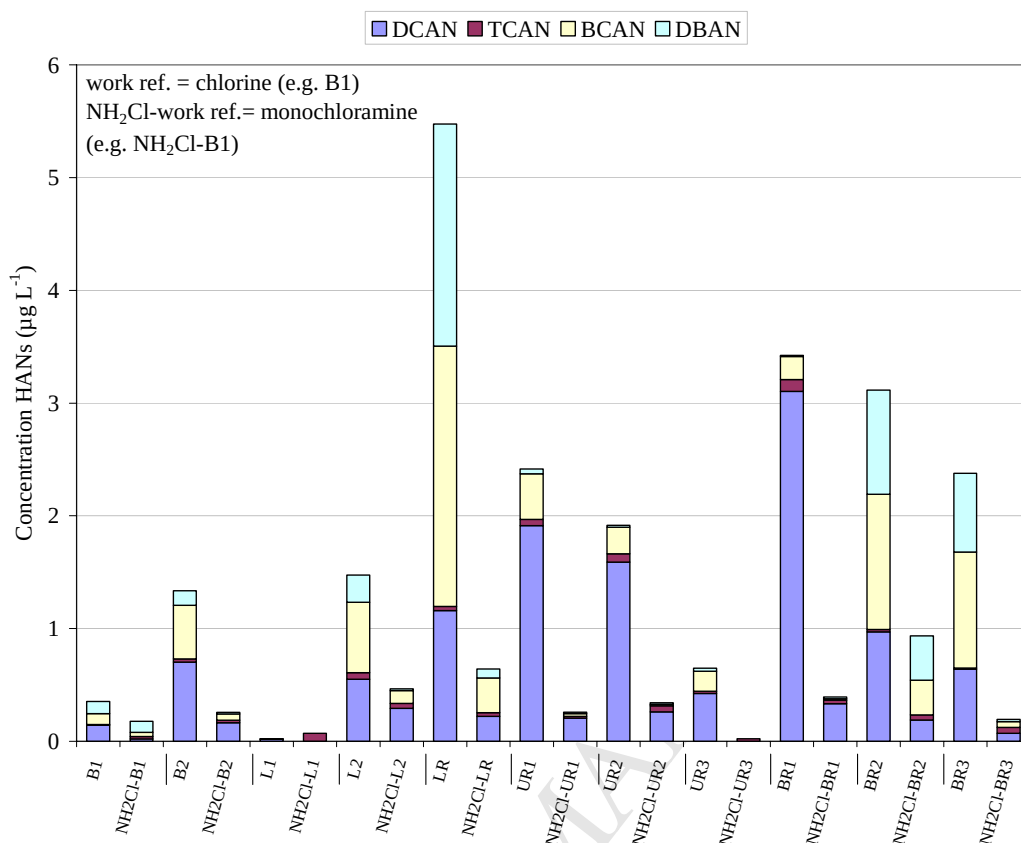


Figure 5. Distribution of HANs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

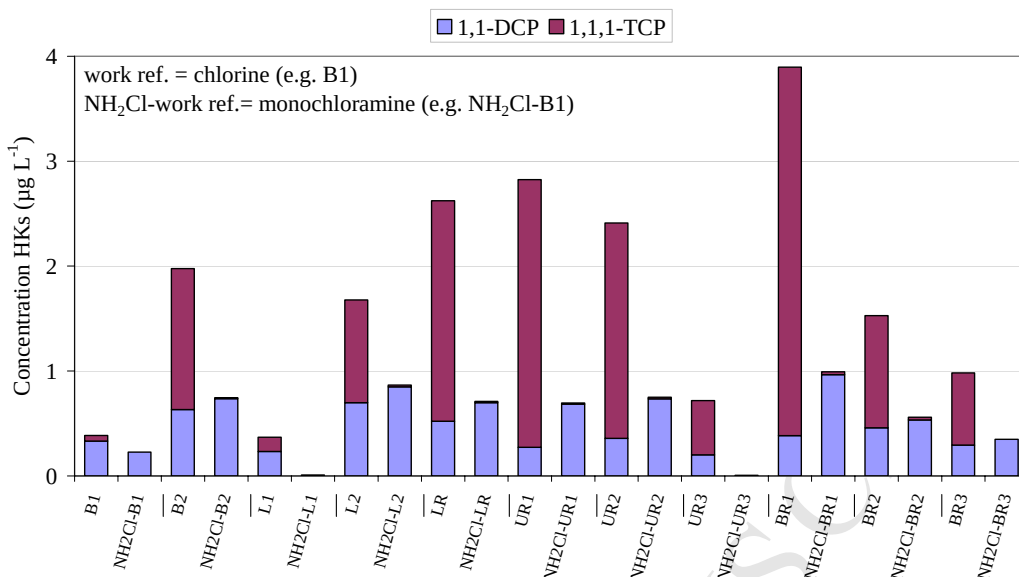


Figure 6. Distribution of HKs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

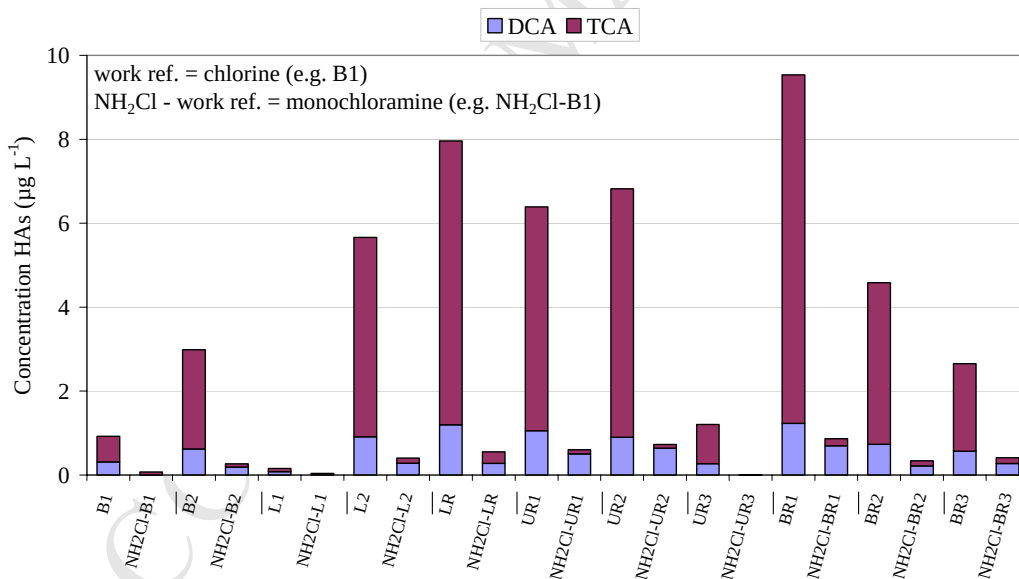


Figure 7. Distribution of HAs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters

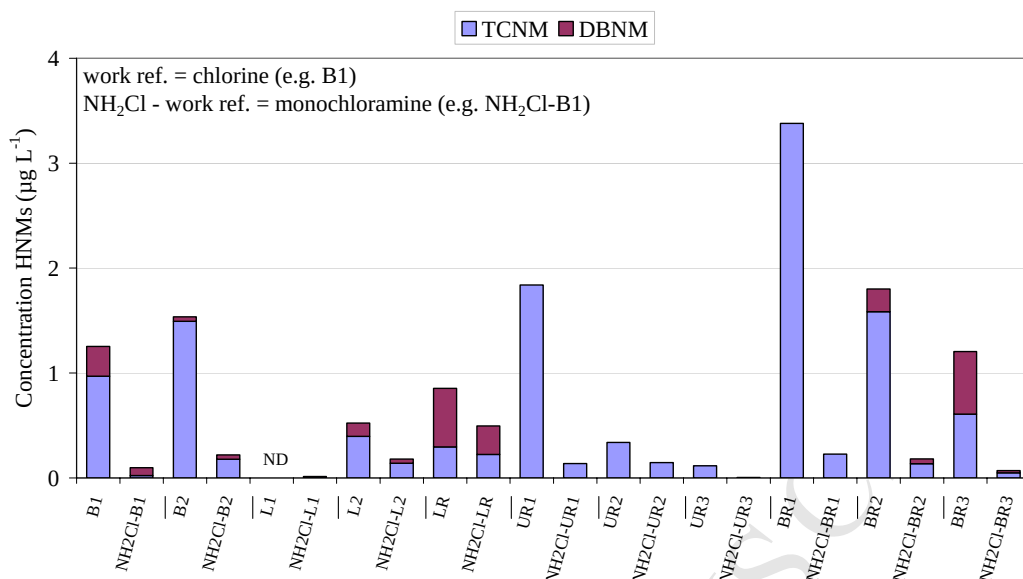


Figure 8. Distribution of HNMs after 24 hours bench scale exposure to chlorine and monochloramine for 11 treated waters (ND – not detected)

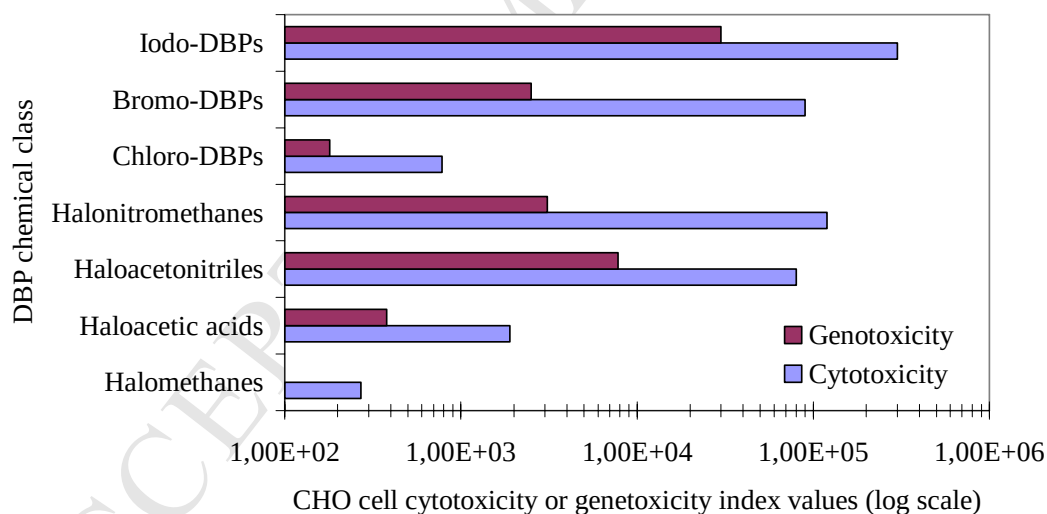


Figure 9. Cytotoxicity and genotoxicity indices for different classes of DBPs and for chloro-, bromo- and iodo-DBPs (Adapted from Plewa et al., 2008)

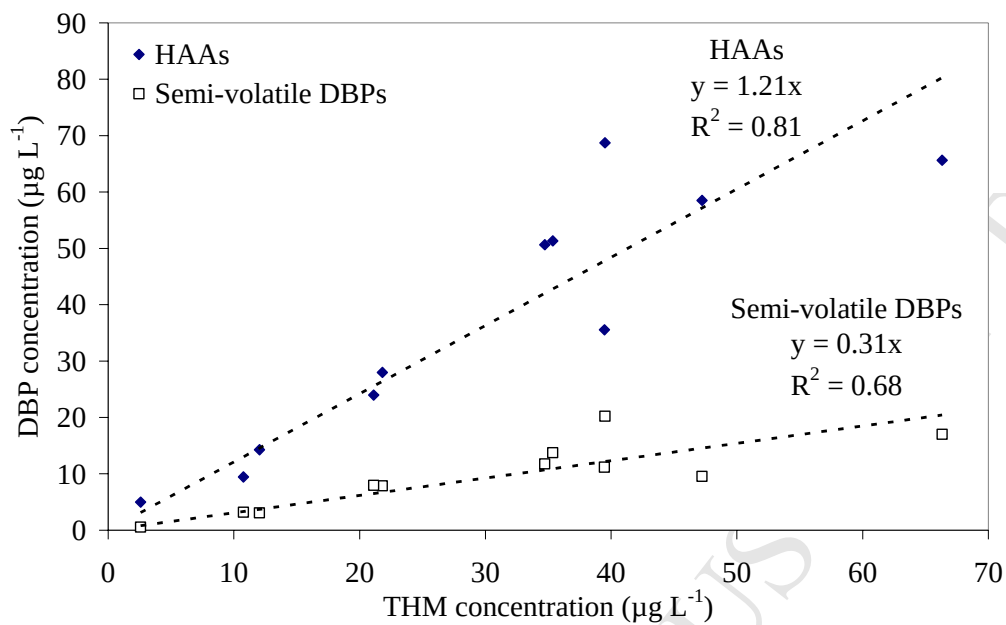


Figure 10. Correlation between THMs with HAAs and the semi-volatile DBPs (chlorine FP tests)

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	<i>Sampling point:</i> Post filter <i>Main process:</i> Filtration	7.8	0.2	0.4	1.5	275	3.5
B2	<i>Sampling point:</i> Post membrane prior to superchlorination <i>Main process:</i> Membrane filtration with pre-oxidation	7.2	1.2	2.2	1.8	42	6.9
LAKE (L)							
L1	<i>Sampling point:</i> Post membrane <i>Main process:</i> Membrane filtration	5.9	1.2	5.5	4.6	31	1.3
L2	<i>Sampling point:</i> Post filter <i>Main process:</i> Coagulation/Direct filtration	6.8	1.2	3.4	2.7	75	16.7
LOWLAND RESERVOIR (LR)							
LR	<i>Sampling point:</i> Post GAC <i>Main process:</i> Ozone/coagulation /GAC	7.8	3.7	5.8	1.6	209	8.9
UPLAND RESERVOIR (UR)							
UR1	<i>Sampling point:</i> Post sand filtration <i>Main process:</i> Coagulation	7.4	1.6	4.2	2.6	44	0.9
UR2	<i>Sampling point:</i> Post filter <i>Main process:</i> Coagulation/filtration	8.9	1.7	4.1	2.4	18	0.9
UR3	<i>Sampling point:</i> Post slow sand filter <i>Main process:</i> Direct filtration	6.2	1.1	5.9	5.4	29	0.9
LOWLAND RIVER (BR)							
BR1	<i>Sampling point:</i> Post GAC <i>Main process:</i> Coagulation/GAC	5.5	2.2	5.3	2.4	14	0.9
BR2	<i>Sampling point:</i> Post GAC <i>Main process:</i> Coagulation/GAC	7.5	1.6	2.9	1.8	310	6.3
BR3	<i>Sampling point:</i> Post GAC <i>Main process:</i> Coagulation/GAC	7.2	1.4	2.4	1.7	108	3.0

ref. – reference

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)	NPOC (mg L ⁻¹)	Coefficient of correlation (R ²)		
		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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