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

25

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 dibromoiodomethane
- 40 DBNM dibromonitromethane
- 41 DBPs disinfection by-products
- 42 DCA dichloroacetaldehyde
- 43 DCAA dichloroacetic acid
- 44 DCAN dichloroacetonitrile
- 45 DCBM dichlorobromomethane
- 46 DCIM dichloroiodomethane
- 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

sum of four THMs does not exceed 100 μ g L⁻¹ with a frequency of sampling dependent 83 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 considering regulating the nine HAAs at 80 μ g L⁻¹ (Cortvriend, 2008) and as such there 86 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 than 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 μ g/L for DCAN, 70 μ g/L for DBAN and 108 10 μ g/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). The presence of bromide in water will also affect the concentration of DBPs as will 114 115 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 with controlled pH, controlled temperature and relatively high chlorine concentration 120 121 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 THM_4 (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 (DBCAA), and tribromomethane (TBAA))

132 plus four HANs (DCAN, trichloroacetonitrile (TCAN), bromochloroacetonitrile 133 (BCAN) and DBAN), two HKs (1,1-dichloropropanone (1,1-DCP) and 1,1,1-134 trichloropropanone (1,1,1-TCP)), two HAs (dichloroacetaldehyde (DCA) and TCA), 135 two HNMs (trichlornitromethane (TCNM) and dibromonitromethane (DBNM)) and two 136 i-THMs (dichloroiodomethane (DCIM) and bromochloroiodomethane (BCIM)). This is 137 the first study that has reported the potential for formation of HAAs, THMs and a range 138 of semi-volatile DBPs in drinking water in England and Wales. It is also the first 139 European study to directly assess what impact the switch from chlorine to 140 monochloramine would have on the concentrations of the DBPs found.

141

142

143 Materials and methods

144 Water samples

145 Treated water samples were collected in July 2008 from 11 water treatment works, 146 spread geographically across England and Wales (Table 1). Samples were collected 147 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) 148 149 using a TOC 5000 Analyser (Shimadzu, Milton Keynes, UK), ultraviolet (UV) 150 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 151 152 was used rather than DOC/TOC as the level of inorganic carbon in some samples was 153 too high to enable accurate DOC/TOC measurement. Bromide and iodine were 154 measured using inductively coupled plasma/mass spectrometry (ICP/MS) (Elan 9000,

155 Perkin Elmer, UK). Total bromine and iodine measured were assumed to be primarily156 bromide and iodide.

157 Sample preparation

Chlorine and monochloramine solutions were prepared following the 4500-Cl B. 158 Iodometric method I and 4500-Cl F. DPD Ferrous Titrimetric Method respectively 159 160 (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 a PTFE-lined cap. Samples were incubated for 24 hours at 20°C in the dark. For the 163 164 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 165 166 chlorine:NPOC ratio of 3:1 by weight. The procedure of monochloraminated samples was the same as that for chlorinated samples. 167

Ammonium chloride at a concentration of 100 mg L^{-1} was used to quench chlorine and monochloramine residual while not degrading HAAs, in particular HAA₃ (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).

174

175 **DBP analytical methods**

HAA₉ 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)

179 (Agilent 6890). THM₄, four HANs, two HKs, two HAs, two HNMs and two i-THMs 180 were extracted with an adapted method from Krasner et al. (2001). Standards for THM₄, 181 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 182 183 (UK). DCA standard was provided by TCI Europe (Belgium); DBNM, DCIM and 184 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 185 186 containing an internal standard. The solvent phase containing the DBPs was separated 187 from the aqueous phase by addition of 10 g of sodium sulphate and 1 g copper sulphate. 188 Then the sample was shaken manually for 3 to 5 minutes. Once settled the top layer was 189 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 190 191 with the detector set at 200°C. Separation was performed by a ZB-1ms column (30 m \times 192 $0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) with a helium carrier gas at a column flow rate of 1.0 mL/min. The 193 initial oven temperature was 35°C and held for 22 minutes followed by a 10°C per 194 minute temperature ramp to 145°C and held for 2 minutes and a final ramp of 20°C per 195 minute ramp to 225°C and held for 10 minutes. The total run time was 49 minutes. The 196 detector temperature was 290°C and the data were collected with a rate of 20 Hz. 197 Quality assurance undertaken showed good reproducibility of the method and limits of detection were typically in the low $\mu g L^{-1}$ range (Table 2). 198

199

200 **Results and discussion**

201 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 NPOC concentration was 1.6 mg L^{-1} with the highest value (3.7 mg L^{-1}) found in LR 205 and the lowest concentration (0.2 mg L^{-1}) in B1. The NPOC concentration of the 206 lowland rivers (mean of 1.7 mg L⁻¹) was similar to that measured in the upland 207 reservoirs (mean of 1.5 mg L^{-1}). SUVA values calculated here ranged from 1.5 m⁻¹ L 208 mg⁻¹ C (B1) to 5.4 m⁻¹ L mg⁻¹ C (UR3). L1 and UR3, with low NPOC values (1.2 and 209 1.1 mg L^{-1} respectively), had high SUVA values of 4.6 and 5.4 m⁻¹ L mg⁻¹ C 210 211 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 direct filtration, not coagulation which is more effective towards removal of 214 hydrophobic material (Sharp et al., 2006). 215

The level of bromine, which we have assumed here to be mainly bromide, ranged from 14 to 310 μ g L⁻¹ (Table 1), with an average concentration of 105 μ g 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 μ g L⁻¹, with an average of 100 μ g 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 μ g 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 μ g 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 μ g L⁻¹. Interestingly the ratio of bromine to

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

228

229 **DBP levels from different water sources**

230 HAAs

231 The concentrations of nine HAAs from the 11 treated waters were quantified after 232 exposure to chlorine and monochloramine (Figure 1). In Figure 1, chlorine data are 233 represented as the treatment work reference only (e.g. B1) and the monochloramine data 234 are shown as NH₂Cl-work reference (e.g. NH₂Cl-B1). It is clear that using 235 monochloramine produced significantly less HAAs (average reduction of 77%) when 236 compared to chlorine. These findings compare well with previous studies that have 237 looked at HAA formation when using preformed monochloramine, typically a 90 to 95% reduction was observed (Cowman and Singer, 1996; Guay et al., 2005). 238

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 μ g L⁻¹, with an average value of 37 μ g 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 μ g L⁻¹.

Across the chlorinated water samples, the major species formed were TCAA (ranging from 1.0 to 40 μ g L⁻¹) and DCAA (ranging from 2.5 to 22 μ g 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

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

252 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 253 254 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 concentration was $\leq 75 \ \mu g \ L^{-1}$, TCAA was predominantly formed whilst when a high 257 concentration of bromine (> 100 μ g L⁻¹) (water samples B1, LR, BR2 and BR3) and an 258 259 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 aqueous chlorine (Westerhoff et al., 2004). Consequently, the NaOCl to the NPOC 261 262 ratio (NaOCI:NPOC), on a mass basis, decreased as the bromine increased. Miller and Uden (1983) amongst others found that at lower NaOCI:NPOC, the relative amount of 263 264 DCAA formed was higher than that of TCAA, which was observed here. For example BR1, with a bromine concentration of 14 μ g L⁻¹, formed 22 μ g L⁻¹ of DCAA and 40 μ g 265 L^{-1} of TCAA, whereas LR, with a bromine concentration of 209 µg L^{-1} formed 16 µg L^{-1} 266 ¹ of DCAA and 12 μ g L⁻¹ of TCAA. 267

When monochloramine was used as the disinfectant the highest concentration of HAAs formed was 14 μ g L⁻¹ (L2, LR and BR1) and the average concentration 8.2 μ g 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%

274 respectively of the total HAA formed. Monohalogenated HAAs (MXAA) were always275 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

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

296
$$BIF = \frac{HAABr_{9} (\mu mol L^{-1})}{HAA_{9} (\mu mol L^{-1})},$$
 Equation 1

where HAABr₉ is the sum of the molar concentrations of bromine incorporated in the nine HAA species and HAA₉ 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 ($\mathbf{R}^2 = 0.72$) than to chlorine ($\mathbf{R}^2 = 0.39$).

303 Overall the results show that BIF increased with increasing bromine concentrations, 304 leading to more brominated HAAs. Also, BIF is higher in chlorinated waters than in 305 monochloraminated waters. Chlorine is a more powerful oxidant and its reaction with 306 bromine to form HOBr and then the formation of brominated HAAs will be faster and 307 more predominant than with monochloramine (Deborde and Von Gunten, 2008).

308 THMs and i-THMs

309 As with the HAAs, shifting from chlorine to monochloramine produced significantly 310 less THMs and the average reduction was 92% (Figure 3). While using chlorine there 311 was considerable variation in THM levels across the 11 waters with concentrations ranging from 2.6 to 66 μ g L⁻¹. The average concentration was 30 μ g L⁻¹, which is 312 similar to the value observed for the HAAs (average of 37 μ g L⁻¹). The lowest 313 314 concentration of THMs was found in L1 and the highest in LR, followed by L2. These 315 results are similar to those for the HAAs, and specifically, the concentration of TCM 316 was similar to that of TCAA in many samples, indicating possible common precursors. For example, in B2, TCM was 13 μ g L⁻¹ and TCAA was 11 μ g L⁻¹, in UR1, both TCM 317 and TCAA were at concentrations of 25 μ g L⁻¹ and in BR1, TCM was 35 μ g L⁻¹ and 318 TCAA was 40 μ g L⁻¹. It was observed that L1 had a lower concentration of THMs than 319 320 L2 (2.6 and 47 μ g L⁻¹ respectively), both waters having the same NPOC values, but L1 321 having a greater SUVA value than L2, which indicates that neither NPOC, nor SUVA

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

325 When using monochloramine the concentrations of THMs were mostly below 1 μ g L⁻¹,

326 aside from B1, LR and BR2. Interestingly, BR2, which had the highest concentration of

327 bromine (310 μ g L⁻¹) could form brominated THMs (13 μ g L⁻¹) even when using

328 monochloramine as a disinfectant.

The concentrations of two i-THMs were also evaluated (Figure 4). The maximum 329 concentration found here was 0.73 μ g L⁻¹ and most concentrations were below the MRL 330 of 0.58 μ g L⁻¹. Cancho et al. (2000) reported average levels lower than 1 μ g L⁻¹ for three 331 332 species (DCIM, BCIM and DBIM) in sand filters and ozonated waters, and Krasner et al., (2006) reported a maximum of 19 μ g L⁻¹ for six i-THMs with DCIM and BCIM 333 334 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.

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

monochloramine were between not detected to 0.89 μ 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.

351 HANs

352 When using chlorine, HANs were detected in all waters and their concentrations were 353 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 μ g L⁻¹, which is in 354 line with the findings of Krasner et al. (2007), who reported levels of dihalogenated 355 HANs between approximately 0.80 μ g L⁻¹ and 6.2 μ g L⁻¹ when using FP tests. DCAN 356 357 was the major HAN formed and contributed up to 56% of the total HAN, followed by 358 BCAN (27%), DBAN (16%) and TCAN (2%). Dihalogenated HANs are reported to be 359 more stable than the trihalogenated HANs by a number of authors (Peters et al., 1990; 360 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 361 362 detected in this study (Croué and Reckhow, 1989).

DCAN was the most abundant species found in chlorinated waters containing levels of 363 bromine $< 50 \ \mu g \ L^{-1}$. In the waters with bromine $\geq 75 \ \mu g \ L^{-1}$ the brominated HANs 364 365 (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 366 HAN in Dutch surface waters with bromide concentrations $\geq 500 \ \mu g \ L^{-1}$. Here the 367 368 lowland waters L1, BR2 and BR3 produced more HANs which is expected as these 369 sources are more likely to contain dissolved organic nitrogen, the main precursor for 370 HANs (Oliver et al., 1983). The speciation observed was again dependent on the presence of bromine. For example BR2, which contains 310 μ g L⁻¹ of bromine, formed 371

mainly BCAN and DBAN (0.31 and 0.39 μ g L⁻¹ respectively), whereas UR2 with a bromine concentration of 18 μ g L⁻¹ formed 0.013 and 0.014 μ g L⁻¹ for both BCAN and DBAN, but 0.26 μ 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 μ g L⁻¹) were formed.

379

380 HKs, HAs and HNMs

The concentrations of the two HKs formed following exposure to chlorine and 381 382 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 μ g L⁻¹, 383 with a mean value of 1.8 μ g L⁻¹. The highest concentration was observed in BR1, 384 385 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 formation of 1,1,1-TCP in the samples is believed to be the result of the excess chlorine 387 388 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 $0.92 \ \mu g \ L^{-1}$ for L1 and the maximum value was $9.5 \ \mu g \ L^{-1}$ for BR1. The average of HAs formed was $4.4 \ \mu g \ L^{-1}$ and this group of DBPs represented

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. Koudjonou et al. (2008) also reported TCA in drinking water made up 60% of the total 399 HA. Ozonation is known to increase the levels of DCA and TCA (Weinberg et al., 400 401 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 potential for DCA (0.62 μ g L⁻¹) and TCA (2.4 μ g L⁻¹) than B1 (0.31 and 0.61 μ g L⁻¹ 403 404 respectively), which has no ozone. The use of monochloramine resulted on average in a 90% decrease in the total HA concentration (Figure 7). 405

The total concentration of HNMs measured after exposure to chlorine ranged from not 406 detected to 3.4 μ g L⁻¹ (Figure 8). The predominant HNM was TCNM and the 407 408 concentrations are in agreement with Krasner et al. (2001) who reported TCNM concentrations of up to 2.0 µg L⁻¹. DBNM was detected here in B1, B2, L2, LR, BR2 409 410 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 highest concentration of HNMs was observed in BR1, a lowland river, followed by 413 414 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 415 416 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.

419

420

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.

433

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 HAAs when chlorine was used (coefficient of correlation $R^2 = 0.82$). The slope of this 437 438 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 different regions in England and Wales ($R^2 = 0.82$ and 0.90), whereas they found a poor 442 443 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, 445 HA, HK, i-THM and HNM) measured after exposure to chlorine (Figure 10). The R^2 446 447 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 448 449 waters (Krasner et al., 1989). This correlation suggests that the control of THM 450 precursors is closely linked to the control of other DBP precursors. As explained by 451 Krasner et al. (1989) this trend is valid for the sum of the measured halogenated DBPs 452 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 453 the regulatory limit of 100 μ g L⁻¹ for the THM₄ would fail a regulation of 80 μ g L⁻¹ for 454 the nine HAAs, currently under consideration by the European Union (Cortvriend, 455 2008). Indeed from the correlation found here, if 100 μ g L⁻¹ of THM₄ would be formed, 456 it would be expected to form 121 μ g L⁻¹ of HAA₉. In the specific waters investigated 457 here, to achieve a concentration of 80 μ g L⁻¹ for HAA₉, THM₄ should be no higher that 458 65 μ g L⁻¹. 459

460

461 Relationships between NPOC, UV and SUVA with DBPs

Relationships between NPOC, UV and SUVA with HAAs, THMs and the semi-volatile 462 463 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 464 to measure than DBPs (Goslan et al., 2002; Parsons et al., 2005; Ates et al., 2007). 465 Firstly, HAAs, THMs and semi-volatile DBPs have been correlated against NPOC and 466 correlation (R² values) between NPOC and HAAs, THMs and the semi-volatile DBPs 467 468 (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^2 469

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478	Conclusions
477	
476	and DBPs was also investigated (Table 3).
475	THMs, HNMs and HKs. No correlations were found between either SUVA or UV_{254}
474	$(R^2 = 0.52)$ (Table 3). However, no correlations were found between NPOC with i-
473	observed that NPOC correlated well with HANs ($R^2 = 0.82$) and moderately with HAS
472	range of water sources. In terms of semi-volatile DBPs as separate species it was
471	correlations observed in a single sample are better than correlations observed from a
470	of 0.86 and 0.87 for HAAs and THMs respectively to NPOC, it is likely that

478 Conclusions

479	٠	The results have shown how all the waters have the potential to form significant				
480		levels of all the DBPs monitored for and that in general a decrease in				
481		concentration was been observed when shifting from chlorine to				
482		monochloramine, the one exception being 1,1-DCP.				

- 483 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 484 hypothesis that they share similar precursor material. 485
- The impact of bromide on the formation of DBPs is well documented in the 486 487 literature and here the data reaffirmed that more bromide species are formed in 488 high bromide-containing waters. For HAAs, brominated species are predominant when bromine was > 100 μ g L⁻¹, whereas the brominated THMs 489 dominated when bromine was \geq 75 µg L⁻¹. 490
- The use of FP test was found here to be unsuitable for the quantification of i-491 • 492 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



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



TCM BDCM DBCM TBM

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)

DCAN TCAN BCAN DBAN



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 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)

Work ref.	Work description	pН	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)								
B 1	Sampling point: Post filter Main process: 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 (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 RES	ERVOI	R (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	

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

ref. - reference

Compound	Average tr ^a (min)	RSD ^b (%)	Detection Limit ^c (µg/L)	MRL ^d (µg/L)	ς
ТСМ	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	

Table 2. Method performance

^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.

		Coefficient of		
		UV	SUVA	
DBPs ($\mu g L^{-1}$)	NPOC (mg L^{-1})	All data	Coagulated	- 50 VA $(\text{m}^{-1} \text{ L} \text{ mg}^{-1} \text{ C})$
		All uata	waters	(m . L mg C)
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

Table 3. Correlation between DBPs and water characteristics

CERES Research Repository

School of Applied Sciences (SAS) (2006-July 2014)

https://dspace.lib.cranfield.ac.uk/

Staff publications (SAS)

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

Bougeard, M. M.

2010-02

Cynthia M.M. Bougeard, Emma H. Goslan, Bruce Jefferson, Simon A. Parsons, Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine, Water Research, Volume 44, Issue 3, February 2010, Pages 729-740 http://dx.doi.org/10.1016/j.watres.2009.10.008. Downloaded from CERES Research Repository, Cranfield University