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**Nitrogenous Disinfection Byproducts in English Drinking Water Supply Systems:  
Occurrence, Bromine Substitution and Correlation Analysis**

Tom Bond<sup>1\*</sup>, Michael R. Templeton<sup>1</sup>, Nurul Hana Mokhtar Kamal<sup>1</sup>, Nigel Graham<sup>1</sup> and  
Rakesh Kanda<sup>2</sup>

1. Department of Civil and Environmental Engineering, Imperial College London, South Kensington campus, London, SW7 2AZ, UK
2. Institute for the Environment, Brunel University London, Uxbridge, UB8 3PH, UK

\*Corresponding author. Email: [t.bond@imperial.ac.uk](mailto:t.bond@imperial.ac.uk). Telephone: +44(0)207 594 6018

## 18 **Abstract**

19 Despite the recent focus on nitrogenous disinfection byproducts in drinking water, there is  
20 limited occurrence data available for many species. This paper analyses the occurrence of  
21 seven haloacetonitriles, three haloacetamides, eight halonitromethanes and cyanogen chloride  
22 in 20 English drinking water supply systems. It is the first survey of its type to compare  
23 bromine substitution factors (BSFs) between the haloacetamides and haloacetonitriles.  
24 Concentrations of the dihalogenated haloacetonitriles and haloacetamides were well  
25 correlated. Although median concentrations of these two groups were lower in chloraminated  
26 than chlorinated surface waters, median BSFs for both in chloraminated samples were  
27 approximately double those in chlorinated samples, which is significant because of the higher  
28 reported toxicity of the brominated species. Furthermore, median BSFs were moderately  
29 higher for the dihalogenated haloacetamides than for the haloacetonitriles. This indicates that,  
30 while the dihalogenated haloacetamides were primarily generated from hydrolysis of the  
31 corresponding haloacetonitriles, secondary formation pathways also contributed. Median  
32 halonitromethane concentrations were remarkably unchanging for the different types of  
33 disinfectants and source waters:  $0.1 \mu\text{g}\cdot\text{mgTOC}^{-1}$  in all cases. Cyanogen chloride only  
34 occurred in a limited number of samples, yet when present its concentrations were higher  
35 than the other N-DBPs. Concentrations of halonitromethanes and cyanogen chloride were not  
36 correlated with any other DBPs.

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38 **Keywords:** haloacetonitriles, haloacetamides, halonitromethanes, cyanogen chloride,  
39 bromine incorporation, chloramines

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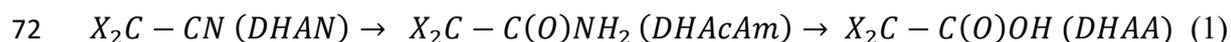
## 41 **1 Introduction**

42 Nitrogenous disinfection byproducts (N-DBPs), including the haloacetonitriles (HANs),  
43 haloacetamides (HAcAms), halonitromethanes (HNMs), cyanogen halides and nitrosamines,  
44 have received much research attention in recent years (Mitch et al., 2009, Bond et al., 2011,  
45 Shah and Mitch 2011). While these species typically occur at lower concentrations in  
46 drinking water than trihalomethanes (THMs, four of which are regulated in the USA, EU and  
47 China) and haloacetic acids (HAAs, five of which are regulated in the USA), there are  
48 concerns that this may be offset by their higher cytotoxicity and genotoxicity (Plewa and  
49 Wagner 2009). One option for water utilities aiming to reduce the formation of THMs and  
50 HAAs is to use chloramines rather than chlorine as the final disinfectant, however, this  
51 change can have the effect of increasing the formation of some N-DBPs, notably cyanogen  
52 chloride (CNCl) (Krasner et al., 1989) and N-nitrosodimethylamine (NDMA) (Choi and  
53 Valentine 2002). Another pertinent factor is that drinking water providers are increasingly  
54 relying on algal- and wastewater-impacted sources, which tend to be enriched in organic  
55 nitrogen compounds known to act as precursor material for many N-DBPs (Mitch et al.,  
56 2009). In general, there is a limited extent of published occurrence data for many N-DBPs in  
57 drinking water, especially the brominated species. The presence of brominated DBPs is of  
58 specific interest because brominated DBPs are typically more cytotoxic and genotoxic than  
59 their chlorinated analogues (Richardson et al., 2007, Yang and Zhang 2013).

60 The dihaloacetonitriles (DHANs) have been reported from chlorinated water supplies since at  
61 least the early 1980s (Oliver 1983, Trehy et al., 1986). A survey of 35 water treatment  
62 facilities later that decade included four HANs (DCAN, BCAN, DBAN and TCAN,  
63 collectively HAN<sub>4</sub>; see Table 1 for abbreviations used), chloropicrin (trichloronitromethane)  
64 and cyanogen chloride (Krasner et al., 1989). These N-DBPs were also monitored in 1997-  
65 1998 during a survey of USA drinking water treatment plants (DWTPs) undertaken as part of  
66 the Information Collection Rule (ICR) (McGuire et al., 2002).

67 The HAcAms are a group of DBPs known to be produced from hydrolysis of the HANs, and  
68 can themselves degrade to the corresponding HAA (Glezer et al., 1999, Reckhow et al.,  
69 2001), as shown below for the dihalogenated species (i.e. the DHANs, DHAcAms and  
70 DHAAs, with X representing a halogen):

71



73

74 The HAcAms were first reported in drinking water during the USA survey of 2000-2002  
75 (Weinberg et al., 2002, Krasner et al., 2006). Up to nine HAcAms have also been  
76 investigated in Chinese raw and treated waters (Chu et al., 2013, Chu et al., 2014). Further, a  
77 laboratory study used isotopically-labelled monochloramine and model precursors to show  
78 that HAcAm formation pathways exist which are separate from HAN hydrolysis and that  
79 HAcAm formation was promoted by chloramination (Huang et al., 2012). It has also been  
80 demonstrated that monochloramine reacts with chloroacetaldehyde to form N,2-  
81 dichloroacetamide (Kimura et al., 2013). Nonetheless, owing to the paucity of literature  
82 comparing concentrations of HAcAms and HANs in real drinking water samples there is still  
83 uncertainty regarding whether HAcAms are primarily produced from HAN hydrolysis, or to  
84 what extent these, and perhaps other, independent formation pathways also contribute.

85 Chloropicrin (trichloronitromethane) has been observed in drinking water since the early days  
86 of DBP research (Merlet et al., 1985). In the 2000-2002 USA nationwide DBP survey, which  
87 sampled 12 DWTPs receiving high precursor loads (measured in terms of high bromide  
88 and/or total organic carbon (TOC)), a total of eight HNMs were monitored, though typically  
89 only 4-5 at individual DWTPs (Weinberg et al., 2002, Krasner et al., 2006). Six HANs, five  
90 HNMs and CNCl were also included in a survey of 11 USA DWTPs receiving waters which  
91 were algal and/or wastewater impacted (Mitch et al., 2009). In their study, Hu et al., (2010)  
92 included all nine HNM group members, while investigating the formation potential of five

93 natural waters under laboratory conditions. They found chloropicrin and  
94 bromodichloronitromethane (BDCNM) were the most commonly encountered species. There  
95 have been fewer surveys to investigate the occurrence of N-DBPs in drinking waters outside  
96 of North America, although four HANs have been monitored in various parts of Europe  
97 (Goslan et al., 2009, Goslan et al., 2014).

98 This paper presents the results of a survey of N-DBPs in 20 English drinking water supply  
99 systems. In contrast to many previous DBP surveys, samples were taken from downstream  
100 distribution systems as well as from the DWTP itself, allowing for an assessment of N-DBP  
101 speciation and concentration trends in distribution. The N-DBPs quantified comprised seven  
102 HANs, three HAcAms, eight HNMs and CNCl (Table 1). The selected water supply systems  
103 included a variety of disinfection methods and source water types (Table S1). THM<sub>4</sub> and  
104 HAA<sub>9</sub> were measured in two and one of the four seasonal sampling rounds, respectively.  
105 NDMA and other nitrosamines were excluded, as this group has previously been the subject  
106 of separate surveys in the UK (Dillon et al., 2008, Templeton and Chen 2010).

107

## 108 **2 Methods**

### 109 **2.1 Sampling approach**

110 Water supply systems selected for sampling included those with DWTPs using ozone, UV  
111 disinfection, chlorine and chloramines for disinfection (Table S1). Six supply systems applied  
112 chloramination in the distribution system, while the rest applied chlorination. Eight treatment  
113 works received water from a lowland catchment, five from an upland catchment and seven  
114 treated groundwater. Twelve treatment works received water from eutrophic sources (a  
115 possible source of organic nitrogen), five had an elevated bromide concentration in the source  
116 waters (defined as  $> 150 \mu\text{g}\cdot\text{L}^{-1}$ , which is considered high in the context of England), and five  
117 had elevated THM levels (defined as  $> 50 \mu\text{g}\cdot\text{L}^{-1}$  in finished water).

118 Sampling was undertaken quarterly from December 2011 to December 2012. Samples were  
119 collected at two locations in each DWTP (pre-disinfection and final treated water) plus three  
120 sites from within the distribution system, chosen to represent near, middle, and distant parts  
121 of the distribution system from the DWTP. There was no blending nor booster  
122 chlor(am)ination in any of the distribution systems during the course of the sampling.  
123 Samples were collected in glass bottles of 1-L (semi-volatile method) or 60-mL (volatile  
124 method) capacity. Prior to sampling 100 mg of ammonium chloride (or 6 mg for the volatile  
125 method) was added to each bottle. Ammonium chloride is recommending in USEPA method  
126 551.1 as a dechlorination agent when analysing HANs and chloropicrin (USEPA 1995). All  
127 samples from the same water supply systems were collected in duplicate on the same day,  
128 stored at below 4°C, extracted within 72 hours and analysed within 15 days of collection.  
129 In addition to the analysed N-DBPs (Table 1), four regulated trihalomethanes (THM<sub>4</sub>) were  
130 measured in Sampling Rounds 1 and 4, and nine haloacetic acids (HAA<sub>9</sub>) were measured in  
131 Sampling Round 4. Initially the intention was also to quantify two other HAcAms (2-  
132 chloroacetamide and 2-bromoacetamide) and cyanogen bromide, but the data for these  
133 compounds was not included because of low analytical recovery. Tribromonitromethane  
134 (bromopicrin) was excluded due to the difficulty in obtaining an analytical standard.

## 135 **2.2 N-DBP analyses**

136 Standards were purchased from either Sigma Aldrich (UK) or CanSyn Chem (Canada),  
137 except for CNCl, which was synthesized based on the procedure of Wu et al. (1998). N-DBPs  
138 were extracted into methyl tert-butyl ether (MTBE), using two modified versions of USEPA  
139 method 551.1 (USEPA 1995) followed by analysis using gas chromatography – mass  
140 spectrometry (GC-MS). Extended versions of these methods, as well as method detection  
141 limits (MDLs), are provided in the supplementary data. CNCl, chloroacetonitrile (CAN), and  
142 trichloroacetonitrile (TCAN) were extracted using the volatile method, while remaining

143 compounds were extracted using the semi-volatile method. For the latter, 400 ±1 mL of  
144 sample was adjusted to pH 4.5 – 5.0, spiked with pre-diluted internal standard solution (d<sub>4</sub>-  
145 1,2 – dichlorobenzene), before 50 g of NaCl and 50 mL MTBE was added. The sample was  
146 then shaken for one hour at 200 rpm. For the Analytical Quality Control (AQC) blank and  
147 spike sample, ultrapure water was spiked with an N-DBP standard solution. After shaking,  
148 samples were allowed to rest for approximately two minutes, before the upper solvent layer  
149 was removed into a 60 mL vial, ensuring as little water as possible was transferred. The vial  
150 was left in a freezer overnight, then filtered using MTBE prewashed glass wool. The 50 mL  
151 extract was concentrated using a concentrator and a nitrogen blow down apparatus, before 2  
152 µL was injected into a GC-MS (Agilent 6890 GC and Agilent 5973 MS) equipped with a  
153 Rtx5 Amine 30 m x 0.25 mm column. For the volatile method, a similar procedure was  
154 followed, except 15 g NaCl and a J&W DB-624, 30 m x 0.25 mm diameter column were used  
155 and the GC conditions varied (refer to the supplementary data).

### 156 **2.3 Other water quality parameters and statistical analysis**

157 For THM<sub>4</sub>, a United Kingdom Accreditation Service (UKAS) headspace – gas  
158 chromatography electron capture detector (GC-ECD) method was used, based on USEPA  
159 Method 524.2 (1992). Meanwhile, HAA<sub>9</sub> were analysed using a modified version of USEPA  
160 Method 552.3 (2003) with quantification by GC-MS. Further information is available in the  
161 supplementary data. In addition to the DBPs analysed, eight water quality parameters (Table  
162 S6) were measured using standard procedures (APHA et al., 2005). Pearson product-moment  
163 correlation coefficients (r), which take values between -1 (total negative correlation) and 1  
164 (total positive correlation), were calculated in Microsoft Excel and used to define linear  
165 relationships between the measured DBPs.

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167

## 168 **3 Results and Discussion**

### 169 **3.1 Overview of water quality from selected supply systems**

170 Median total organic carbon (TOC) and bromide concentrations in final waters from the  
171 DWTPs (i.e. post disinfection but pre-distribution system) were  $1.7 \text{ mg}\cdot\text{L}^{-1}$  and  $48 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ ,  
172 respectively (Table S7). Both these parameters are important factors in DBP formation and  
173 were far lower in each case than respective raw water values -  $5.8 \text{ mg}\cdot\text{L}^{-1}$  and  $120 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  -  
174 from the USA survey of 2000-2002 (Krasner et al., 2006), where DWTPs were specifically  
175 selected because they received high precursor loadings. This likely explains why occurrence  
176 of THM<sub>4</sub> was slightly lower in the English waters with a median concentration of  $20 \text{ }\mu\text{g}\cdot\text{L}^{-1}$   
177 in final waters (Table S7), versus  $31 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  in the USA (Krasner et al., 2006). However,  
178 HAA<sub>9</sub> exhibited the opposite trend, with the median concentration being  $48 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  in final  
179 water in the current study (Table S7) and  $34 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  in the USA survey (Krasner et al., 2006).  
180 The major contributor to HAA<sub>9</sub> formation were the trihaloacetic acids (THAAs), which had a  
181 median concentration of  $26 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  in final waters.

182 Note that only DBP concentrations above the respective minimum detection limit (MDL)  
183 have been reported and used in the data analysis, which may therefore represent a  
184 conservative estimation of typical DBP concentrations in English drinking waters. Another  
185 important factor to note when comparing DBP data between multiple surveys are differences  
186 in disinfection protocols. In England water companies generally maintain chlorine at  $<0.5$   
187  $\text{mg}\cdot\text{L}^{-1}$  in distribution systems (DWI 2010), whereas in the USA up to  $4 \text{ mg}\cdot\text{L}^{-1}$  (as either free  
188 chlorine or chloramines) is permitted (USEPA 1998). This is emphasised by the median free  
189 chlorine concentrations in final water and distribution samples -  $0.5$  and  $0.2 \text{ mg}\cdot\text{L}^{-1}$ ,  
190 respectively - from the current study (Table S7). In contrast, chlorine concentrations in final  
191 waters from five DWTPs in the USA 2000-2002 survey which maintained a free chlorine  
192 residual during distribution ranged from  $1.69 - 4.0 \text{ mg}\cdot\text{L}^{-1}$  (Weinberg et al., 2002).

### 193 3.2 Haloacetonitriles (HANs)

194 Three dihalogenated HANs – DCAN, BCAN and DBAN - were the most frequently recorded  
195 N-DBPs, being detected above MDLs in 496, 534 and 513 samples, respectively, out of 759  
196 samples analysed in total (Table 2). The median concentration of DCAN in all disinfected  
197 samples was  $0.9 \mu\text{g}\cdot\text{L}^{-1}$  (Table 2), whereas Krasner et al. (2006) reported an equivalent value  
198 of  $1.0 \mu\text{g}\cdot\text{L}^{-1}$  in final waters. The maximum DCAN concentration of  $4.4 \mu\text{g}\cdot\text{L}^{-1}$  (Table 2) was  
199 the same as reported by Goslan et al. (2009) in Scottish drinking water and much lower than  
200 the maximum of  $12.0 \mu\text{g}\cdot\text{L}^{-1}$  reported in the USA (Krasner et al., 2006). All the measured  
201 HANs, as well as the other N-DBPs recorded, occurred at levels well below the World Health  
202 Organisation (WHO) guidelines of  $20 \mu\text{g}\cdot\text{L}^{-1}$  and  $70 \mu\text{g}\cdot\text{L}^{-1}$  for DCAN and DBAN,  
203 respectively (WHO 2011). TCAN was not recorded at all in the survey at levels above the  
204 MDLs, while DBCAN was only recorded in 46 samples, up to a maximum of  $0.7 \mu\text{g}\cdot\text{L}^{-1}$ ,  
205 illustrating trihalogenated HANs are rare in drinking water at detectable levels.

206 Median and maximum concentrations for the sum of  $\text{HAN}_4$  were respectively 2.8 and 12.1  
207  $\mu\text{g}\cdot\text{L}^{-1}$  in all disinfected samples, in comparison to equivalent values of 3.0 and  $14.0 \mu\text{g}\cdot\text{L}^{-1}$  in  
208 the USA (Krasner et al., 2006). Thus,  $\text{HAN}_4$  occurred at similar concentrations as have been  
209 reported in surveys in other countries. Median concentrations of  $\text{HAN}_4$  increased slightly in  
210 distribution, relative to final water concentrations, from 2.6 to  $2.8 \mu\text{g}\cdot\text{L}^{-1}$  respectively (Table  
211 2), while the maximum  $\text{HAN}_4$  concentration recorded came from the distribution sample of a  
212 supply system disinfected with ozonation-chlorination (Table S8).

213 Although CAN and BAN were only recorded above MDLs in respectively 9 and 22 samples,  
214 they reached maxima of  $1.9$  and  $3.8 \mu\text{g}\cdot\text{L}^{-1}$  in distribution (Table 2). Occurrence of these two  
215 monohalogenated HANs was not linked to high concentrations of other HANs, as shown by  
216 the absence of any notable correlations involving CAN and BAN (Table S9). Concentrations  
217 of the HANs were linked to those of the HAAs, although not the THMs, with correlation

218 coefficients of  $r = 0.66$  and  $0.36$ , respectively (Table 3). Relationships between HANs and  
219 HAcAms are discussed in Section 3.4.

### 220 **3.3 Haloacetamides (HAcAms)**

221 Respective median concentrations for the two dihalogenated HAcAms - DCACAm and  
222 DBACAm - were  $0.6$  and  $0.7 \mu\text{g}\cdot\text{L}^{-1}$ , with equivalent maxima being  $4.5$  and  $5.1 \mu\text{g}\cdot\text{L}^{-1}$  (Table  
223 2). For comparison, DCACAm concentrations from a pre-chloramination DWTP in China  
224 reached a maximum of  $1.8 \mu\text{g}\cdot\text{L}^{-1}$  (Chu et al., 2011). Interestingly, TCACAm ( $n=203$ ) was  
225 detected far more commonly than TCAN ( $n=0$ ), albeit only at concentrations of up to  $1.7$   
226  $\mu\text{g}\cdot\text{L}^{-1}$ . MDLs for TCAN ( $0.5 \mu\text{g}\cdot\text{L}^{-1}$ ; Table S5) were slightly higher than for TCACAm ( $0.1$ -  
227  $0.3 \mu\text{g}\cdot\text{L}^{-1}$ ; Table S5), which partly explains this difference, though there were still 50  
228 TCACAm samples  $\geq 0.5 \mu\text{g}\cdot\text{L}^{-1}$  as TCAN (the maximum TCAN MDL). Furthermore, the  
229 median sum of DCACAm and DBACAm in samples where TCACAm was present above the  
230 MDL was  $1.4 \mu\text{g}\cdot\text{L}^{-1}$ , versus an equivalent value of  $1.1 \mu\text{g}\cdot\text{L}^{-1}$  in samples without TCACAm.  
231 This reveals TCACAm that tended to occur more in samples with higher concentrations of the  
232 dihalogenated HAcAms. Table 3 supports this, and suggests its occurrence was also linked to  
233 that of DCAN, given that there were weak correlation coefficients,  $r = 0.55$  and  $0.61$ , between  
234 TCACAm and DCAN, and between TCACAm and DCACAm, respectively. TCACAm and  
235 TCAN were also undetectable in most water samples at the aforementioned Chinese pre-  
236 chloramination DWTP (Chu et al., 2011). Median, seventy-fifth percentile and maximum  
237 concentrations of both DCACAm and DBACAm (and the sum of HAcAms) all increased  
238 slightly in distribution, relative to final water concentrations (Table 2). Seventy-fifth  
239 percentile and maximum concentrations of TCACAm were also higher in distribution than in  
240 final waters. As with the HANs, HAcAm concentrations were moderately correlated with  
241 HAA<sub>9</sub> and THAAs, respective correlations coefficients being  $r = 0.58$  and  $0.64$ . Neither  
242 group exhibited any notable correlations with other groups of DBPs (Table 3).

### 243 **3.4 Relationships between HANs and HAcAms**

244 There has been debate in recent literature about whether the HANs and HAcAms share  
245 common precursors and formation routes, or alternatively whether the HAcAms are also  
246 generated independently from the HANs. In the current study there were strong correlations  
247 between DCAN and DCAcAm, between DBAN and DBAcAm, and between the HAcAms  
248 and HANs, of  $r = 0.77$ ,  $0.90$  and  $0.76$ , respectively (Table 3). These coefficients are  
249 consistent with the premise that HAcAms are predominantly generated from hydrolysis of  
250 HANs.

251 Huang et al. (2012) found that HAcAms were associated with chloramination, rather than  
252 chlorination, of various natural organic matter types. In the selected supply systems the  
253 pattern of HANs and HAcAms generated by the different disinfection methods was similar  
254 (Figure 1). The highest concentrations of both groups were from waters disinfected using  
255 ozone-chlorine, which is not something highlighted previously. However, when the DBPs  
256 were normalised against organic carbon, i.e. by plotting them in  $\mu\text{g}\cdot\text{mgTOC}^{-1}$ , then it  
257 becomes apparent this is mainly an artefact of the ozone-chlorine DWTPs receiving waters  
258 with high precursor loadings (Figure 1).

259 Moreover, for both groups of DBPs, TOC-normalised median concentrations tended to be  
260 higher in chlorinated rather than chloraminated waters. In chlorinated waters, median HAN  
261 concentrations ranged from  $1.4 \mu\text{g}\cdot\text{mgTOC}^{-1}$  in lowland chlorinated waters to  $2.2$   
262  $\mu\text{g}\cdot\text{mgTOC}^{-1}$  in the single DWTP using UV-chlorination as the disinfection method. In  
263 comparison, median HAN concentrations from lowland ozone-chloramine and upland  
264 chloramine DWTPs were  $1.1$  and  $0.5 \mu\text{g}\cdot\text{mgTOC}^{-1}$ , respectively (Figure 1). The distribution  
265 system using chloramines to disinfect a groundwater was atypical, as it generated slightly  
266 higher amounts of HANs, on a central tendency basis, than the chlorinated groundwaters:  $1.7$   
267 and  $1.6 \mu\text{g}\cdot\text{mgTOC}^{-1}$ , respectively, with both lower than the UV-chlorine disinfected

268 groundwater (Figure 1). These data demonstrate that HAN and HAcAm formation (in  
269  $\mu\text{g}\cdot\text{mgTOC}^{-1}$ ) from the (chlorinated and chloraminated) groundwaters was comparable to that  
270 from the chlorinated surface waters.

271 Although the occurrence of HAcAms present a similar pattern as the HANs, the median  
272 concentrations of the HAcAms were consistently lower, representing from 25-63% of the  
273 median concentrations (in  $\mu\text{g}\cdot\text{mgTOC}^{-1}$ ) of the HANs (Figure 1). Thus, except for the  
274 groundwaters, when comparing across the same water categories, median HAcAm  
275 concentrations were lower in the chloraminated than the chlorinated distribution systems.

### 276 **3.5 Bromine incorporation into DBPs**

277 Bromine substitution factors (BSFs) for DBAN + DCAN versus DBAcAm + DCaAm are  
278 plotted in Figure 2. BSFs measure the proportion of bromine incorporated into a group of  
279 DBPs, relative to the total amount of substituted chlorine and bromine (with concentrations of  
280 halogen and DBPs in moles). As calculated by Hua and Reckhow (2012) they always vary  
281 between 0 (only the chlorinated member of the relevant group recorded) and 1 (only the  
282 brominated member recorded):

283

$$284 \text{ Bromine substitution factor (BSF)} = [\text{DBP-Br}]/[\text{DBP-(Cl+Br)}] \quad (2)$$

285

286 There were trend lines with  $R^2$  values of 0.60 and 0.85 in chloraminated and chlorinated  
287 waters, respectively (Figure 2), or of 0.80 when all samples were analysed together. Figure 2  
288 also shows a higher number of DBAcAm + DCaAm data points with a BSF of 1.0. This  
289 indicates that the amount of bromine incorporation in DBAcAm + DCaAm was higher than  
290 in DBAN + DCAN. Table 4 confirms this, as median BSF values in all chlorinated samples  
291 were 0.30 for DBAN + DCAN and 0.36 for DBAcAm + DCaAm. In chloraminated  
292 samples BSFs were dramatically higher for both groups: 0.60 and 0.70, respectively. To the

293 authors' knowledge, this is the first time that HAcAm and HAN BSFs have been compared in  
294 drinking water.

295 The finding that median DBAcAm + DCaAm BSFs were respectively 20 and 17% higher  
296 in chlorinated and chloraminated waters than median DBAN + DCAN BSFs is consistent  
297 with the presence of two (or more) pathways contributing to HAcAm formation, one (or  
298 more) of which had a higher level of bromine substitution than in HANs. Nonetheless, the  
299 strong correlations noted above between DCAN + DCaAm and between DBAN +  
300 DBAcAm, as well the comparable impact of different disinfection methods; indicate that  
301 these were of secondary importance to HAN hydrolysis.

302 Median THM BSFs also increased between chlorinated and chloraminated samples, from  
303 0.29 to 0.39, respectively (Table 4). In contrast, median BSFs for the dihaloacetic acids  
304 (DHAAs) were uniform between the two disinfectants (Table 4). This is congruent with the  
305 model developed by Duirk and Valentine (2007), which showed that chlorine incorporated  
306 into DHAAs more effectively than bromine during chloramination.

307 The enhanced BSFs calculated for the chloraminated waters – manifest for the DHANs,  
308 dihaloacetamides (DHAcAms) and THMs - are linked to multiple factors. The first is that the  
309 chloraminated waters had typically higher bromide levels: the median concentration being 60  
310  $\mu\text{g}\cdot\text{L}^{-1}$ , versus 29  $\mu\text{g}\cdot\text{L}^{-1}$  in chlorinated samples (Table 4). Secondly, small amounts of free  
311 chlorine present during chloramination, rather than the chloramines themselves, may be  
312 important to the generation of chloramination DBPs (Cowman and Singer 1996). The  
313 simultaneous presence of chloramines, bromamines, bromochloroamine, free chlorine and  
314 free bromine during chloramination in the presence of bromide makes identifying the active  
315 oxidation and halogenation agents in DBP formation intractable (Diehl et al., 2000, Duirk and  
316 Valentine 2007). Nonetheless, chlorination BSFs are known to peak at low chlorine doses  
317 (Hua and Reckhow 2012), when the bromine/chlorine ratio is highest, such as occurring

318 when small amounts of free chlorine are present during chloramination. However, other  
319 authors have demonstrated that monochloramine, rather than free chlorine, is predominantly  
320 responsible for DBP formation during chloramination. Notably, experiments undertaken with  
321 isotopically-labelled monochloramine by Yang et al. (2010) demonstrated that, during  
322 monochloramination of two amino acids and Suwannee River natural organic matter, the  
323 majority of the nitrogen in the DCAN formed originated from monochloramine, rather than  
324 the organic precursor. Another study used a kinetic model to propose that bromochloramine  
325 and monobromamine were predominantly responsible for brominated DBP formation during  
326 the chloramination of simulated drinking waters, whereas hypobromous acid only accounted  
327 for a minor amount (Zhai et al., 2014). The dramatic increase in BSFs for dihalogenated  
328 HANs and HAcAms upon chloramination highlights the presence of pathways with increased  
329 bromine incorporation relative to those operating during chlorination. It is established that  
330 both chlorination and chloramination of amino acids leads to either aldehyde or nitrile  
331 formation and can ultimately generate DHANs, DHAcAms and DHAAs (Yang et al., 2010).  
332 Based on the product distribution during model compound experiments, chloramination  
333 favours aldehyde formation over nitrile formation (Yang et al., 2010, Bond et al., 2014b), so  
334 this is likely to be a relevant mechanism.

335 In Table 4, BSFs are shown for Round 4 of sampling separately, since this was the only  
336 round to incorporate both THMs and HAAs and as bromide concentrations were lower than  
337 from across the whole survey. During Round 4 median bromide concentrations were 22 and  
338  $34 \mu\text{g}\cdot\text{L}^{-1}$  in chlorinated and chloraminated samples respectively, versus equivalent values of  
339 29 and  $60 \mu\text{g}\cdot\text{L}^{-1}$  across the whole survey (Table 4). The order of median chlorination BSFs  
340 in Round 4 for DBP groups where all the chloro- and/or bromo- species were quantified was  
341 THAAs > DHAAs > DHANs > THMs. For comparison, BSFs during chlorination of a single  
342 raw water between pH 5 and 7 were in the order DHANs > THMs & DHAAs > THAAs (Hua

343 and Reckhow 2012). Another study using a raw water showed that maxima BSFs were in the  
344 order of THMs > DHAAs and THAAs (Bond et al., 2014a). This demonstrates that relative  
345 BSFs for different DBP groups can vary, which is linked to study-specific differences in  
346 precursor characteristics and oxidation conditions.

347 Overall, with the exception of DHAAs, BSFs were always higher in chloraminated rather  
348 than chlorinated samples. This pattern was most striking for DCAN + DBAN and DCACAm  
349 + DBACAm, where median BSFs were respectively 100 and 94% higher in chloraminated  
350 than in chlorinated samples. The higher bromine incorporation in chloraminated water supply  
351 systems is significant because of the higher cytotoxicity and genotoxicity of brominated  
352 DBPs than the corresponding chlorinated species (Plewa and Wagner 2009).

### 353 **3.6 Halonitromethanes (HNMs)**

354 HNMs of any description were observed less frequently than the HANs and HACams, with  
355 only BNM and chloropicrin found in over 100 samples (Table 2). Concentrations of DHNMs  
356 and THNMs were always close to MDLs, which contributes to the sum of HNMs being  
357 generally low. Median and maximum concentrations for the sum of HNMs were 0.2 and 7.0  
358  $\mu\text{g}\cdot\text{L}^{-1}$  (Table 2). In contrast, Krasner et al. (2006), reported equivalent values of 3.0 and 10.0  
359  $\mu\text{g}\cdot\text{L}^{-1}$ . Part of the explanation for this difference is that tribromonitromethane (bromopicrin)  
360 was not included in the current study, as it was in the USA survey, albeit only being observed  
361 at low concentrations. Further, median bromide concentrations in final waters were 48  $\mu\text{g}\cdot\text{L}^{-1}$   
362 (Table S7), compared with 120  $\mu\text{g}\cdot\text{L}^{-1}$  in raw waters of the 12 US DWTPs (Krasner et al.,  
363 2006). Therefore, bromopicrin concentrations are unlikely to have exceeded those in the USA  
364 and it can be supposed that overall HNM concentrations were lower in the English waters.

365 A similar finding can be reached by comparing chloropicrin concentrations, where respective  
366 median and maximum values were 0.2 and 0.5  $\mu\text{g}\cdot\text{L}^{-1}$  in the current study, lower than the  
367 values of 0.4 and 2.0  $\mu\text{g}\cdot\text{L}^{-1}$  in the USA survey of 2000-2002 (Krasner et al., 2006), which

368 were in turn less than the 0.5 and 7.6  $\mu\text{g}\cdot\text{L}^{-1}$  in the USA survey of impacted DWTPs (Mitch  
369 et al., 2009) (Table 2). Moreover, Mitch et al. (2009) reported a maximum of 2.0  $\mu\text{g}\cdot\text{L}^{-1}$  for  
370 the sum of three DHNMs, versus 0.5  $\mu\text{g}\cdot\text{L}^{-1}$  in the current study.

371 The HNMs recorded at the highest concentrations in the current study were actually the two  
372 monohalogenated species, CNM and BNM, at 3.5 and 3.8  $\mu\text{g}\cdot\text{L}^{-1}$  respectively (Table 2), with  
373 these maxima coming from the same sample. This situation was somewhat atypical, as  
374 appearances of CNM and BNM were not strongly correlated with one another (Table 3). In  
375 fact, there were no notable correlation coefficients between any of the individual HNM  
376 species (Table 3). More broadly, the sum of the HNMs was also not correlated with any other  
377 DBPs, except for CNM (Table 3), showing that the HNMs did not share do not share key  
378 precursors and formation pathways with the other DBPs monitored. Previous research has  
379 shown chloropicrin was stable in the presence of free chlorine or monochloramine at pH 5,  
380 whereas in the presence of monochloramine or free chlorine at pH 9 it had a half-life of ~3  
381 days (Joo and Mitch, 2007). In the current study, there was no trend for concentrations of  
382 HNMs to decline in distribution. Median concentrations of BNM, DCNM and chloropicrin  
383 were the same in both final waters and distribution samples, while median concentrations of  
384 DBNM increased slightly and those of CNM decreased slightly (Table 2).

385 On a central tendency basis, TOC-normalised concentrations of HNMs were remarkably  
386 unchanging with different types of disinfectants and source waters, being 0.1  $\mu\text{g}\cdot\text{mgTOC}^{-1}$  in  
387 all cases (Figure 3). For comparison, Lee et al., (2007) reported that equal amounts of  
388 chloropicrin were found upon chlorination and chloramination of natural organic matter  
389 fractions, while chloropicrin yields were slightly higher from chlorination than  
390 chloramination of nitrogen-rich isolates (Dotson et al., 2009).

391 However, differences are evident in the seventy-fifth percentile and maximum concentrations  
392 of HNMs (plotted as  $\mu\text{g}\cdot\text{mgTOC}^{-1}$ ), with the former being highest in the only UV-chlorine

393 disinfected distribution system, a groundwater, while the maximum came from a distribution  
394 sample of another groundwater-fed supply system. It is known that oxidation with ozone  
395 (Hoigne and Bader 1988, Hu et al., 2010) or UV irradiation (Reckhow et al., 2010, Shah et  
396 al., 2011) prior to chlorination enhances HNM formation. The former was not evident from  
397 the ozonation-chlorination English distribution systems (Figure 3), presumably because they  
398 contained lower amounts of HNM precursor material and/or due to differences in operational  
399 parameters during ozonation.

### 400 **3.7 Cyanogen chloride (CNCl)**

401 Occurrences of CNCl were erratic, since it was only recorded above MDLs in 148 out of 759  
402 samples analysed, yet median and maximum concentrations were higher than the other N-  
403 DBPs, at 4.5 and 18.4  $\mu\text{g}\cdot\text{L}^{-1}$ , respectively (Table 2). Its concentrations were not correlated  
404 with any of the other DBPs (Table 3), indicating a disparate group of precursors was involved  
405 in its formation.

406 On a central tendency basis the highest CNCl concentrations amongst the different types of  
407 sources waters and disinfectants were formed in the chloraminated groundwater, where a  
408 median value of 4.3  $\mu\text{g}\cdot\text{mgTOC}^{-1}$  was recorded (Figure 4). This agrees with other research  
409 demonstrating that CNCl formation was enhanced in chloraminated water, something noted  
410 from the 1980s onwards (Krasner et al., 1989). Nonetheless, high concentrations were also  
411 generated on occasion in chlorinated waters, as shown by a median value of 3.5  $\mu\text{g}\cdot\text{mgTOC}^{-1}$   
412 in chlorinated upland waters and the highest concentration from any sample (in  $\mu\text{g}\cdot\text{mgTOC}^{-1}$ )  
413 being from a chlorinated lowland water (Figure 4). However, when DBP formation was  
414 reported in  $\mu\text{g}\cdot\text{L}^{-1}$ , the maximum concentration of CNCl came from a chloraminated  
415 distribution system (Table S8). Median, seventy-fifth percentile and maximum concentrations  
416 of CNCl all increased slightly in distribution, relative to final water concentrations: from 4.4,  
417 7.5 and 12.6 to 4.6, 8.0 and 18.4  $\mu\text{g}\cdot\text{L}^{-1}$ , respectively (Table 2).

418

#### 419 **4 Conclusions**

420 This study determined, for the first time, the occurrence of seven HANs, three HAcAms,  
421 eight HNMs and CNCl in 20 English drinking water supply systems. New knowledge  
422 regarding the correlations between N-DBPs groups and their bromine substitution arose,  
423 including:

- 424 • Bromine substitution into haloacetonitriles and haloacetamides was higher in  
425 chloraminated waters than in chlorinated waters. Median BSFs for DCAN + DBAN  
426 and for DCaAm + DBaAm were respectively 100 and 94% higher in  
427 chloraminated than in chlorinated samples. Thus, although HAN and HAcAm  
428 formation was overall lower in chloraminated waters, a dramatic shift to more  
429 brominated species occurred.
- 430 • Bromine substitution was higher in haloacetamides than in haloacetonitriles. Median  
431 DBaAm + DCaAm BSFs were respectively 20 and 17% higher in chlorinated and  
432 chloraminated waters than median DBAN + DCAN BSFs.
- 433 • Relationships between concentrations of DCAN and DCaAm and between DBAN  
434 and DBaAm showed correlation coefficients of  $r = 0.77$  and  $0.90$ , respectively.  
435 Overall, this study indicates that dihalogenated HAcAms were primarily generated  
436 from hydrolysis of the corresponding HAN, though secondary formation pathways  
437 also contributed. In addition, TCaAm was detected far more frequently than TCAN.
- 438 • HNMs and CNCl were not correlated with any of the other DBP groups included in  
439 this study, suggesting disparate groups of precursors were involved in their  
440 formation than the other DBPs monitored.

441

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450

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