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

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Abstract

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

Keywords: haloacetonitriles, haloacetamides, halonitromethanes, cyanogen chloride, bromine incorporation, chloramines

1 Introduction

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

The dihaloacetonitriles (DHANs) have been reported from chlorinated water supplies since at least the early 1980s (Oliver 1983, Trehy et al., 1986). A survey of 35 water treatment facilities later that decade included four HANs (DCAN, BCAN, DBAN and TCAN, collectively HAN_4; see Table 1 for abbreviations used), chloropicrin (trichloronitromethane) and cyanogen chloride (Krasner et al., 1989). These N-DBPs were also monitored in 1997-1998 during a survey of USA drinking water treatment plants (DWTPs) undertaken as part of the Information Collection Rule (ICR) (McGuire et al., 2002).

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

$$X_2C-CN\ (DHAN) \rightarrow\ X_2C-C(O)NH_2\ (DHAcAm) \rightarrow\ X_2C-C(O)OH\ (DHAA) \quad (1)$$

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

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

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

This paper presents the results of a survey of N-DBPs in 20 English drinking water supply systems. In contrast to many previous DBP surveys, samples were taken from downstream distribution systems as well as from the DWTP itself, allowing for an assessment of N-DBP speciation and concentration trends in distribution. The N-DBPs quantified comprised seven HANs, three HAcAms, eight HNMs and CNCl (Table 1). The selected water supply systems included a variety of disinfection methods and source water types (Table S1). THM_4 and HAA_9 were measured in two and one of the four seasonal sampling rounds, respectively. NDMA and other nitrosamines were excluded, as this group has previously been the subject of separate surveys in the UK (Dillon et al., 2008, Templeton and Chen 2010).

2 Methods

2.1 Sampling approach

Water supply systems selected for sampling included those with DWTPs using ozone, UV disinfection, chlorine and chloramines for disinfection (Table S1). Six supply systems applied chloramination in the distribution system, while the rest applied chlorination. Eight treatment works received water from a lowland catchment, five from an upland catchment and seven treated groundwater. Twelve treatment works received water from eutrophic sources (a possible source of organic nitrogen), five had an elevated bromide concentration in the source waters (defined as > 150 $\mu g \cdot L^{-1}$, which is considered high in the context of England), and five had elevated THM levels (defined as > 50 $\mu g \cdot L^{-1}$ 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_4) were
130 measured in Sampling Rounds 1 and 4, and nine haloacetic acids (HAA_9) 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

compounds were extracted using the semi-volatile method. For the latter, 400 ±1 mL of sample was adjusted to pH 4.5 – 5.0, spiked with pre-diluted internal standard solution (d_4-1,2 – dichlorobenzene), before 50 g of NaCl and 50 mL MTBE was added. The sample was then shaken for one hour at 200 rpm. For the Analytical Quality Control (AQC) blank and spike sample, ultrapure water was spiked with an N-DBP standard solution. After shaking, samples were allowed to rest for approximately two minutes, before the upper solvent layer was removed into a 60 mL vial, ensuring as little water as possible was transferred. The vial was left in a freezer overnight, then filtered using MTBE prewashed glass wool. The 50 mL extract was concentrated using a concentrator and a nitrogen blow down apparatus, before 2 µL was injected into a GC-MS (Agilent 6890 GC and Agilent 5973 MS) equipped with a Rtx5 Amine 30 m x 0.25 mm column. For the volatile method, a similar procedure was followed, except 15 g NaCl and a J&W DB-624, 30 m x 0.25 mm diameter column were used and the GC conditions varied (refer to the supplementary data).

2.3 Other water quality parameters and statistical analysis

For THM_4, a United Kingdom Accreditation Service (UKAS) headspace – gas chromatography electron capture detector (GC-ECD) method was used, based on USEPA Method 524.2 (1992). Meanwhile, HAA_9 were analysed using a modified version of USEPA Method 552.3 (2003) with quantification by GC-MS. Further information is available in the supplementary data. In addition to the DBPs analysed, eight water quality parameters (Table S6) were measured using standard procedures (APHA et al., 2005). Pearson product-moment correlation coefficients (r), which take values between -1 (total negative correlation) and 1 (total positive correlation), were calculated in Microsoft Excel and used to define linear relationships between the measured DBPs.

3 Results and Discussion

3.1 Overview of water quality from selected supply systems

Median total organic carbon (TOC) and bromide concentrations in final waters from the DWTPs (i.e. post disinfection but pre-distribution system) were 1.7 $mg.L^{-1}$ and 48 $\mu g \cdot L^{-1}$, respectively (Table S7). Both these parameters are important factors in DBP formation and were far lower in each case than respective raw water values - 5.8 $mg.L^{-1}$ and 120 $\mu g \cdot L^{-1}$ - from the USA survey of 2000-2002 (Krasner et al., 2006), where DWTPs were specifically selected because they received high precursor loadings. This likely explains why occurrence of THM_4 was slightly lower in the English waters with a median concentration of 20 $\mu g \cdot L^{-1}$ in final waters (Table S7), versus 31 $\mu g \cdot L^{-1}$ in the USA (Krasner et al., 2006). However, HAA_9 exhibited the opposite trend, with the median concentration being 48 $\mu g \cdot L^{-1}$ in final water in the current study (Table S7) and 34 $\mu g \cdot L^{-1}$ in the USA survey (Krasner et al., 2006). The major contributor to HAA_9 formation were the trihaloacetic acids (THAAs), which had a median concentration of 26 $\mu g \cdot L^{-1}$ in final waters.

Note that only DBP concentrations above the respective minimum detection limit (MDL) have been reported and used in the data analysis, which may therefore represent a conservative estimation of typical DBP concentrations in English drinking waters. Another important factor to note when comparing DBP data between multiple surveys are differences in disinfection protocols. In England water companies generally maintain chlorine at <0.5 $mg \cdot L^{-1}$ in distribution systems (DWI 2010), whereas in the USA up to 4 $mg \cdot L^{-1}$ (as either free chlorine or chloramines) is permitted (USEPA 1998). This is emphasised by the median free chlorine concentrations in final water and distribution samples - 0.5 and 0.2 $mg \cdot L^{-1}$, respectively - from the current study (Table S7). In contrast, chlorine concentrations in final waters from five DWTPs in the USA 2000-2002 survey which maintained a free chlorine residual during distribution ranged from 1.69 – 4.0 $mg \cdot L^{-1}$ (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 $\mu g \cdot L^{-1}$ (Table 2), whereas Krasner at al. (2006) reported an equivalent value
198 of 1.0 $\mu g \cdot L^{-1}$ in final waters. The maximum DCAN concentration of 4.4 $\mu g \cdot L^{-1}$ (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 $\mu g \cdot L^{-1}$ 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 $\mu g \cdot L^{-1}$ and 70 $\mu g \cdot L^{-1}$ 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 $\mu g \cdot L^{-1,}$
205 illustrating trihalogenated HANs are rare in drinking water at detectable levels.
206 Median and maximum concentrations for the sum of HAN_4 were respectively 2.8 and 12.1
207 $\mu g \cdot L^{-1}$ in all disinfected samples, in comparison to equivalent values of 3.0 and 14.0 $\mu g \cdot L^{-1}$ in
208 the USA (Krasner et al., 2006). Thus, HAN_4 occurred at similar concentrations as have been
209 reported in surveys in other countries. Median concentrations of HAN_4 increased slightly in
210 distribution, relative to final water concentrations, from 2.6 to 2.8 $\mu g \cdot L^{-1}$ respectively (Table
211 2), while the maximum 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 $\mu g \cdot L^{-1}$ 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

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

3.3 Haloacetamides (HAcAms)

Respective median concentrations for the two dihalogenated HAcAms - DCAcAm and DBAcAm - were 0.6 and 0.7 $\mu g \cdot L^{-1}$, with equivalent maxima being 4.5 and 5.1 $\mu g \cdot L^{-1}$ (Table 2). For comparison, DCAcAm concentrations from a pre-chloramination DWTP in China reached a maximum of 1.8 $\mu g \cdot L^{-1}$ (Chu et al., 2011). Interestingly, TCAcAm (n=203) was detected far more commonly than TCAN (n=0), albeit only at concentrations of up to 1.7 $\mu g \cdot L^{-1}$. MDLs for TCAN (0.5 $\mu g \cdot L^{-1}$; Table S5) were slightly higher than for TCAcAm (0.1-0.3 $\mu g \cdot L^{-1}$; Table S5), which partly explains this difference, though there were still 50 TCAcAm samples ≥ 0.5 $\mu g \cdot L^{-1}$ as TCAN (the maximum TCAN MDL). Furthermore, the median sum of DCAcAm and DBAcAm in samples where TCAcAm was present above the MDL was 1.4 $\mu g \cdot L^{-1}$, versus an equivalent value of 1.1 $\mu g \cdot L^{-1}$ in samples without TCAcAm. This reveals TCAcAm that tended to occur more in samples with higher concentrations of the dihalogenated HAcAms. Table 3 supports this, and suggests its occurrence was also linked to that of DCAN, given that there were weak correlation coefficients, r = 0.55 and 0.61, between TCAcAm and DCAN, and between TCAcAm and DCAcAm, respectively. TCAcAm and TCAN were also undetectable in most water samples at the aforementioned Chinese pre-chloramination DWTP (Chu et al., 2011). Median, seventy-fifth percentile and maximum concentrations of both DCAcAm and DBAcAm (and the sum of HAcAms) all increased slightly in distribution, relative to final water concentrations (Table 2). Seventy-fifth percentile and maximum concentrations of TCAcAm were also higher in distribution than in final waters. As with the HANs, HAcAm concentrations were moderately correlated with HAA_9 and THAAs, respective correlations coefficients being r = 0.58 and 0.64. Neither group exhibited any notable correlations with other groups of DBPs (Table 3).

3.4 Relationships between HANs and HAcAms

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

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

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

groundwater (Figure 1). These data demonstrate that HAN and HAcAm formation (in μg·mgTOC^{-1}) from the (chlorinated and chloraminated) groundwaters was comparable to that from the chlorinated surface waters.

Although the occurrence of HAcAms present a similar pattern as the HANs, the median concentrations of the HAcAms were consistently lower, representing from 25-63% of the median concentrations (in μg·mgTOC^{-1}) of the HANs (Figure 1). Thus, except for the groundwaters, when comparing across the same water categories, median HAcAm concentrations were lower in the chloraminated than the chlorinated distribution systems.

3.5 Bromine incorporation into DBPs

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

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

There were trend lines with R^2 values of 0.60 and 0.85 in chloraminated and chlorinated waters, respectively (Figure 2), or of 0.80 when all samples were analysed together. Figure 2 also shows a higher number of DBAcAm + DCAcAm data points with a BSF of 1.0. This indicates that the amount of bromine incorporation in DBAcAm + DCAcAm was higher than in DBAN + DCAN. Table 4 confirms this, as median BSF values in all chlorinated samples were 0.30 for DBAN + DCAN and 0.36 for DBAcAm + DCAcAm. In chloraminated 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 + DCAcAm 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 + DCAcAm 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 $\mu g \cdot L^{-1}$, versus 29 $\mu g \cdot L^{-1}$ 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 $\mu g \cdot L^{-1}$ in chlorinated and chloraminated samples respectively, versus equivalent values of
339 29 and 60 $\mu g \cdot L^{-1}$ 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 $\mu g \cdot L^{-1}$ (Table 2). In contrast, Krasner et al. (2006), reported equivalent values of 3.0 and 10.0
359 $\mu g \cdot L^{-1}$. 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 $\mu g \cdot L^{-1}$
362 (Table S7), compared with 120 $\mu g \cdot L^{-1}$ 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 $\mu g \cdot L^{-1}$ in the current study, lower than the
367 values of 0.4 and 2.0 $\mu g \cdot L^{-1}$ in the USA survey of 2000-2002 (Krasner et al., 2006), which

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

The HNMs recorded at the highest concentrations in the current study were actually the two monohalogenated species, CNM and BNM, at 3.5 and 3.8 $\mu g \cdot L^{-1}$ respectively (Table 2), with these maxima coming from the same sample. This situation was somewhat atypical, as appearances of CNM and BNM were not strongly correlated with one another (Table 3). In fact, there were no notable correlation coefficients between any of the individual HNM species (Table 3). More broadly, the sum of the HNMs was also not correlated with any other DBPs, except for CNM (Table 3), showing that the HNMs did not share do not share key precursors and formation pathways with the other DBPs monitored. There was a weak correlation between chloropicrin and trichloromethane (chloroform), of r = 0.60 (Table S9). Previous research has shown chloropicrin was stable in the presence of free chlorine or monochloramine at pH 5, whereas in the presence of monochloramine or free chlorine at pH 9 it had a half-life of ~3 days (Joo and Mitch, 2007). In the current study, there was no trend for concentrations of HNMs to decline in distribution. Median concentrations of BNM, DCNM and chloropicrin were the same in both final waters and distribution samples, while median concentrations of DBNM increased slightly and those of CNM decreased slightly (Table 2).

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

393 However, differences are evident in the seventy-fifth percentile and maximum concentrations
394 of HNMs (plotted as $\mu g \cdot mgTOC^{-1}$), with the former being highest in the only UV-chlorine
395 disinfected distribution system, a groundwater, while the maximum came from a distribution
396 sample of another groundwater-fed supply system. It is known that oxidation with ozone
397 (Hoigne and Bader 1988, Hu et al., 2010) or UV irradiation (Reckhow et al., 2010, Shah et
398 al., 2011) prior to chlorination enhances HNM formation. The former was not evident from
399 the ozonation-chlorination English distribution systems (Figure 3), presumably because they
400 contained lower amounts of HNM precursor material and/or due to differences in operational
401 parameters during ozonation.

402 **3.7 Cyanogen chloride (CNCl)**

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

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

418 of CNCl all increased slightly in distribution, relative to final water concentrations: from 4.4,
419 7.5 and 12.6 to 4.6, 8.0 and 18.4 $\mu g \cdot L^{-1}$, respectively (Table 2).
420
421 **4 Conclusions**
422 This study determined, for the first time, the occurrence of seven HANs, three HAcAms,
423 eight HNMs and CNCl in 20 English drinking water supply systems. New knowledge
424 regarding the correlations between N-DBPs groups and their bromine substitution arose,
425 including:
426 • Bromine substitution into haloacetonitriles and haloacetamides was higher in
427 chloraminated waters than in chlorinated waters. Median BSFs for DCAN + DBAN
428 and for DCAcAm + DBAcAm were respectively 100 and 94% higher in
429 chloraminated than in chlorinated samples. Thus, although HAN and HAcAm
430 formation was overall lower in chloraminated waters, a dramatic shift to more
431 brominated species occurred.
432 • Bromine substitution was higher in haloacetamides than in haloacetonitriles. Median
433 DBAcAm + DCAcAm BSFs were respectively 20 and 17% higher in chlorinated and
434 chloraminated waters than median DBAN + DCAN BSFs.
435 • Relationships between concentrations of DCAN and DCAcAm and between DBAN
436 and DBAcAm showed correlation coefficients of r = 0.77 and 0.90, respectively.
437 Overall, this study indicates that dihalogenated HAcAms were primarily generated
438 from hydrolysis of the corresponding HAN, though secondary formation pathways
439 also contributed. In addition, TCAcAm was detected far more frequently than TCAN.
440 • CNCl and the sum of HNMs were not correlated with any of the other DBP groups
441 included in this study, suggesting disparate groups of precursors where involved in
442 their formation than the other DBPs monitored.

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