

1 Formation of nitrogenous disinfection by-products in 10 chlorinated and 2 chloraminated drinking water supply systems

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13 Abstract

14 The presence of nitrogenous disinfection by-products (N-DBPs) in drinking water supplies is a
15 public health concern, particularly since some N-DBPs have been reported to be more toxic than the
16 regulated trihalomethanes and haloacetic acids. In this paper, a comprehensive evaluation of the
17 presence of N-DBPs in 10 drinking water supply systems in Western Australia is presented. A suite
18 of 28 N-DBPs, including *N*-nitrosamines, haloacetonitriles (HANs), haloacetamides (HAAMs) and
19 halonitromethanes (HNMs), were measured and evaluated for relationships with bulk parameters in
20 the waters before disinfection. A number of N-DBPs were frequently detected in disinfected waters,
21 although at generally low concentrations (<10 ng/L for *N*-nitrosamines and <10 µg/L for other N-
22 DBPs), and below health guideline values where they exist. While there were no clear relationships
23 between N-DBP formation and organic nitrogen in the pre-disinfection water, N-DBP
24 concentrations were significantly correlated with dissolved organic carbon (DOC) and ammonia,
25 and these, in addition to high bromide in one of the waters led to elevated concentrations of
26 brominated HANs (26.6 µg/L of dibromoacetonitrile). There were significant differences in the
27 occurrence of all classes of N-DBPs between chlorinated and chloraminated waters, except for
28 HNMs, which were detected at relatively low concentrations in both water types. Trends observed
29 in one large distribution system suggest that N-DBPs can continue to form or degrade within
30 distribution systems, and redosing of disinfectant may cause further by-product formation.

31 Key Words

32 Nitrogenous disinfection by-products, *N*-Nitrosamines, Haloacetonitriles, Haloacetamides,
33 Chloramination, Distribution system

34 **Introduction**

35 Drinking water disinfection is of utmost importance for water treatment to eliminate waterborne
36 pathogens and prevent transmission of waterborne diseases (Hrudey, 2009). However, it results in
37 unintended side effects when disinfectants, such as chlorine or monochloramine, react with natural
38 organic matter (NOM) and/or bromide/iodide to form disinfection by-products (DBPs). Drinking
39 water DBPs have emerged as a public health issue since they have been implicated with adverse
40 health effects in reproduction and cancer (Richardson, 2003). Over 600 DBPs have been identified
41 but only a relatively small proportion has been quantified in drinking waters (Krasner et al., 2006;
42 Richardson et al., 2007). Furthermore, the DBPs identified so far account for less than 50% of the
43 total organic halides in disinfected drinking water (Krasner et al., 2006), indicating that there is still
44 a large percentage of unknown DBPs, which are potentially more toxic than conventional DBPs
45 such as trihalomethanes (THMs) and haloacetic acids (HAAs). One particular group of DBPs that
46 have not been extensively studied are nitrogenous DBPs (N-DBPs), which may form from water
47 sources with a high content of dissolved organic nitrogen, especially when impacted by wastewater
48 or algae (Bond et al., 2012; Lee et al., 2007). Major classes of N-DBPs that have been previously
49 identified include the *N*-nitrosamines, haloacetonitriles (HANs), halonitromethanes (HNMs) and
50 haloacetamides (HAAs) (Liew et al., 2012a). Interest in N-DBPs has grown steadily in recent
51 years since they are perceived to be a greater human health risk than the presently regulated THMs
52 and HAAs. For example, *in-vitro* toxicological studies have shown that HANs, HNMs and HAAs
53 are much more genotoxic and cytotoxic than the regulated HAAs (Muellner et al., 2007; Plewa et
54 al., 2008; Plewa et al., 2004). This has led to the conclusion that N-DBPs are more toxic than non-
55 nitrogenous DBPs. In addition, *N*-nitrosamines, such as *N*-nitrosodimethylamine (NDMA), have
56 become a significant health concern in drinking water supplies due to their high carcinogenic
57 potency (CDPH, 2011; IARC, 1978). The World Health Organisation (WHO) recommends
58 drinking water guideline values for dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN) and
59 NDMA of 20 µg/L, 70 µg/L and 100 ng/L, respectively. In the United States, federal drinking water
60 guideline levels have been established for DCAN and DBAN, at 6 µg/L and 20 µg/L, respectively
61 (USEPA, 2007). The latest version of the Australian Drinking Water Guidelines (ADWG) includes
62 guideline values for only one N-DBP (NDMA) at a value of 100 ng/L (NHMRC-NRMMC, 2011).
63 Various health guidelines for the presence of NDMA in drinking water have been adopted by
64 agencies in other parts of the world. The California Department of Public Health has advised
65 notification levels of 10 ng/L for NDMA and 2 other *N*-nitrosamines, with future regulation under
66 consideration (CDPH, 2011), while Health Canada has recommended a drinking water guideline of

67 40 ng/L for NDMA (HealthCanada, 2012), and the Drinking Water Inspectorate for England and
68 Wales has set a “wholesomeness limit” of 10 ng/L for NDMA (DWI, 2008).

69 The typical concentrations of N-DBPs identified in drinking waters have been previously reviewed
70 (Bond et al., 2011; Liew et al., 2012a). The *N*-nitrosamines (particularly NDMA) and HANs have
71 been reported more frequently, and studies of other N-DBPs in drinking waters are rare. The
72 occurrence of NDMA and other *N*-nitrosamines in drinking water is associated with a range of
73 factors, including the presence of precursors (Bond et al., 2012; Gerecke & Sedlak, 2003), use of
74 nitrogen-containing polymers and ion exchange resins in water treatment (Kemper et al., 2009;
75 Najm & Trussell, 2001; Wilczak et al., 2003), bromide concentration (Luh & Mariñas, 2012), as
76 well as residence time in distribution systems (Charrois et al., 2004; Charrois et al., 2007; Zhao et
77 al., 2006). Reported concentrations of *N*-nitrosamines in chlorinated or chloraminated drinking
78 waters are typically 10 ng/L or less, but can be in excess of 100 ng/L with longer residence times in
79 the distribution system (Bond et al., 2011; Charrois et al., 2007). Higher NDMA concentrations
80 have been frequently observed with the use of chloramination rather than chlorination (Charrois et
81 al., 2007; Goslan et al., 2009; Liew et al., 2015; Najm & Trussell, 2001; Russell et al., 2012).

82
83 Studies dating back to the 1970s have shown that HANs are nearly ubiquitous in chlorinated
84 drinking waters, with the dihalogenated species being the most prevalent (Krasner et al., 1989;
85 Krasner et al., 2006; Liew et al., 2012a; Oliver, 1983; Williams et al., 1997). Concentrations of
86 DCAN, DBAN and bromochloroacetonitrile (BCAN) in drinking waters are generally below 10
87 µg/L (Goslan et al., 2009; Krasner et al., 1989; Williams et al., 1997), but concentrations as high as
88 41 µg/L have been recorded during the U.S. EPA Information Collection Rule, for the sum of 4
89 HANs, DCAN, DBAN, BCAN and trichloroacetonitrile (TCAN) (McGuire et al., 2002).
90 Concentrations of HNMs in drinking waters are typically lower than the HANs and are mostly
91 below 5 µg/L (Simpson & Hayes, 1998; Weinberg et al., 2002; Williams et al., 1997), but have
92 been shown to increase when ozonation is applied before chlorine or chloramine treatment (Hoigné
93 & Bader, 1988; Krasner et al., 2006; Weinberg et al., 2002). Haloacetamides have been reported at
94 low µg/L concentrations (<10 µg/L) in chlorinated and chloraminated drinking waters (Krasner et
95 al., 2006; Weinberg et al., 2002). Like the HANs, the dihalogenated species, particularly
96 dichloroacetamide (DCAAm), have been found to be the major HAAM species (Chu et al., 2012;
97 Krasner et al., 2006). The occurrence of these N-DBPs in drinking water distribution systems is
98 complicated by the fact that the presence of residual chlorine can cause N-DBPs, such as HANs and
99 HAAMs, to degrade after initial formation (Reckhow et al., 2001).

100

101 To date there are few studies that have focussed on the occurrence of a broad range of N-DBPs in
102 drinking water systems. Selected N-DBPs have been included in surveys of DBPs in drinking water
103 systems in the United States (Krasner et al., 2006; McGuire et al., 2002; Weinberg et al., 2002),
104 Canada (Shanks et al., 2013; Williams et al., 1997) and Europe (Goslan et al., 2009; Goslan et al.,
105 2014). A more comprehensive study has been recently reported in English water supply systems,
106 where the occurrence of 19 halogenated N-DBPs was analysed, with focus on brominated N-DBPs
107 (Bond et al., 2015). In Australia, one early survey of drinking waters in 16 nationwide locations
108 focused on halogenated DBPs, and included only some HANs and one HNM, chloropicrin
109 (Simpson & Hayes, 1998), while our more recent publication reports NDMA concentrations
110 Australia-wide (Liew et al., 2015).

111 The aim of this study was to investigate the formation and occurrence of a suite of 28 N-DBPs,
112 including haloacetonitriles (HANs), halonitromethanes (HNMs), haloacetamides (HAAs) and the
113 non-halogenated *N*-nitrosamines, in ten different drinking water systems in Western Australia. This
114 represents the first comprehensive survey of N-DBP occurrence in Australia, and one of only a few
115 such studies in the world. Drinking water treatment supply schemes were selected for sampling
116 based on factors predicted to influence the formation of N-DBPs, such as their use of nitrogen-
117 containing treatment polymers (e.g. polyacrylamide) and/or ion exchange resins during treatment,
118 and the organic nitrogen content and/or dissolved organic carbon (DOC) content in their source
119 waters. The majority of drinking water systems in Western Australia utilise chlorine disinfection,
120 but extensive sampling was also undertaken throughout the Goldfields and Agricultural Water
121 Supply Scheme (GAWSS), which is Western Australia's only chloraminated water supply and
122 spans over several thousand kilometres of distribution pipeline in total. Occurrence data was used
123 to: 1) identify the most frequently occurring and most abundant N-DBPs, 2) examine relationships
124 between N-DBP formation and bulk water parameters, 3) compare N-DBPs in chlorinated and
125 chloraminated systems, and 4) examine changes in N-DBPs in an extensive chloraminated
126 distribution system.

127 **Methodology**

128 Sampling Locations

129 Sample sites included 4 groundwater treatment plants utilising chlorination for disinfection in
130 metropolitan Perth (GW1-GW4), 5 surface water treatment plants using chlorination in regional
131 Western Australia (SW1-SW5), and 1 drinking water treatment plant and distribution system using
132 chloramination (with monochloramine and chlorine addition along the distribution system) in
133 regional Western Australia (GAWSS). Site descriptions and factors of interest for selected sample

134 sites are presented in the Electronic supplementary material (ESM) (Table S1). Sampling occurred
135 between June 2010 – May 2012. Each site was typically sampled at the raw water stage, post-
136 disinfection (at the treatment plant outlet), and in the distribution system. Some chlorinated sites
137 performed treatment for NOM removal (e.g. coagulation/flocculation followed by filtration) prior to
138 chlorination. At a later stage in the survey, samples after these initial treatment steps (denoted ‘post-
139 pretreatment’ samples in this work, i.e. after NOM removal processes) were also included to
140 provide better representation of the water quality just before disinfection. Therefore some of the
141 sample sites (GW1, GW2, GW3, GW4 and SW4) were sampled on 2 occasions to include the post-
142 pretreatment sample point (when not included in the first instance). All dates of sampling are
143 included in ESM Table S1. The GAWSS was sampled more intensively than the chlorinated
144 systems due to the larger size of the distribution network, and a total of 14 points were sampled
145 within this system. Figure 1 shows a schematic diagram of all the samples taken along the main
146 GAWSS pipeline, as well as along 2 extension pipelines emanating from the main pipeline.

147 Sample Collection

148 Quenching agents were used in sample bottles to quench disinfectant residuals at the time of
149 sampling, and were appropriate for each group of analytes. For *N*-nitrosamines, samples were
150 collected in 1 L amber glass bottles containing ascorbic acid (20 mg/L) for quenching. For HANs,
151 samples were collected in 60 mL clear vials containing 1 g of solid mixture (of ascorbic acid (0.24
152 g), KH_2PO_4 (198 g) and Na_2HPO_4 (2.0 g)). For HNMs and HAAs, samples were collected in 60
153 mL clear vials containing ammonium chloride (100 mg/L). We have previously recommended the
154 use of ammonium chloride as a quenching agent for HNMs and HAAs (Liew et al., 2012b),
155 owing to decomposition of brominated HNMs during application of other quenching agents. Note
156 that ammonium chloride is a quenching agent specifically for chlorine, as it converts a free chlorine
157 residual to chloramines (Kristiana et al., 2014). In the case of chloramination, the chloramine
158 residual is not quenched per se, but rather the decrease in $\text{Cl}_2\text{:N}$ ratio of the water has been shown to
159 lower DBP formation (Chu et al., 2013). Single samples were analysed as soon as possible to
160 minimise analyte degradation. For DOC, samples were collected in 40 mL clear vials containing
161 sodium sulphite (25 mg/L). For other water quality parameters, samples for bromide and iodide
162 were collected in 50 mL plastic bottles containing sodium sulphite (25 mg/L), while samples for
163 nitrogen composition (ammonia, nitrate, nitrite, total nitrogen) were collected in 100 mL plastic
164 bottles.

165 Sample bottles containing the appropriate quenching agent were filled with no headspace, kept at
166 4°C in an ice box and transported back to the laboratory for immediate analysis, or refrigerated in
167 the dark at 4°C until the time of extraction, which was typically within 24 hours. Trip and field

168 blanks containing ultrapure water and respective quenching agents were also included during each
169 sampling event to identify any contamination through the sampling process, transport and storage.
170 Trip blanks remained unopened until analysis, and field blanks were opened at each sampling
171 location.

172 Water Quality Parameters of Samples

173 Field measurements were undertaken during each sampling event using portable meters for chlorine
174 and/or monochloramine residuals (Pocket ColorimeterTM II, Hach Co., USA), and pH, conductivity
175 and temperature (HQ40d, Hach Co., USA). DOC was analysed using a Shimadzu TOC-VWS
176 Analyser (Schimadzu, Tokyo, Japan) utilising persulfate oxidation. All samples for DOC were
177 filtered through a 0.45 µm filter before measurement. All waters were sent to an external laboratory
178 for measurement of other water quality parameters by standard methods including ammonia, nitrate,
179 nitrite, total nitrogen, bromide and iodide.

180 Analyses of N-DBPs

181 A total of 28 N-DBPs were measured. This included 8 halogenated nitriles (dibromoacetonitrile
182 (DBAN), dichloroacetonitrile (DCAN), chloroacetonitrile (MCAN), trichloroacetonitrile (TCAN),
183 bromoacetonitrile (MBAN), bromochloroacetonitrile (BCAN), 2,2-dichloropropanenitrile and 2,2-
184 dibromobutanenitrile), 7 HNMs (trichloronitromethane (chloropicrin), tribromonitromethane
185 (bromopicrin), dichloronitromethane (DCNM), dibromonitromethane (DBNM),
186 bromochloronitromethane (BCNM), bromodichloronitromethane (BDCNM),
187 dibromochloronitromethane (DBCNM)), 5 HAAs (chloroacetamide (CAAm), bromoacetamide
188 (BAAm), dichloroacetamide (DCAAm), dibromoacetamide (DBAAm), trichloroacetamide
189 (TCAAm)) and 8 *N*-nitrosamines (*N*-nitrosodimethylamine (NDMA), *N*-nitrosoethylmethylamine
190 (NEMA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosodi-*n*-
191 butylamine (NDBA), *N*-nitrosopiperidine (NPIP), *N*-nitrosopyrrolidine (NPYR), *N*-
192 nitrosomorpholine (NMOR)). N-DBPs were analysed in 3 separate analytical methods using gas
193 chromatography-mass spectrometry (GC-MS) following different organic extraction methods for
194 different DBP groups. Halogenated nitriles were analysed using a method described by Kristiana et
195 al. (2012), employing solid-phase microextraction (SPME) followed by GC-MS. HNMs and
196 HAAs were analysed together in a method described by Liew et al. (2012b), using liquid-liquid
197 extraction followed by GC-MS. *N*-Nitrosamines were analysed according to the method of Charrois
198 et al. (2004), with minor modifications, employing solid-phase extraction (SPE) followed by GC-
199 MS operating with ammonia positive chemical ionization. Method detection limits were determined
200 for every analytical run using triplicate measurements of low concentration standards (USEPA,
201 2005) and are presented in the ESM (Table S2).

202 **Results & Discussion**

203 N-DBPs in Chlorinated Drinking Water Systems

204 *Water Quality and N-DBP Occurrence*

205 An overview of pre-disinfection water characteristics in the 9 chlorinated systems surveyed is
206 presented in the ESM (Table S3). For those plants that utilised pre-treatment for DOC removal,
207 waters were characterised after pretreatment and just before disinfection, to provide a direct
208 comparison for subsequent N-DBP formation upon disinfection. Thus, ‘pre-disinfection water’
209 refers to the raw water (for sites that do not perform any pretreatment before disinfection) or post-
210 pretreatment water (for sites that perform some form of NOM removal before disinfection).

211 Table 1 summarises the detection frequencies of those N-DBPs that were detected at least once in
212 chlorinated systems, separated into groundwater or surface water source waters. None of the N-
213 DBPs were detected in trip and field blanks, with the exception of NDMA which was detected on 3
214 separate occasions (6-255 ng/L). However, this was presumed to be due to contamination of the
215 bottles or laboratory ultrapure water used, as NDMA concentrations in samples were always below
216 detection on these occasions. No N-DBPs were detected in raw waters, with the exception of
217 NDMA and NDBA, which were detected at close to their limits of detection on 3 separate
218 occasions. All 6 HANs, 2 HNMs (DCNM and BCNM), 3 HAAs (CAAm, DBAAm, DCAAm)
219 and 3 *N*-nitrosamines (NDMA, NDBA and NDPA) were detected at least once after chlorination.
220 For both groundwaters and surface waters, HANs were the most frequently detected N-DBPs,
221 particularly the dihalogenated species (BCAN, DBAN and DCAN) (83-100% detection in samples
222 after chlorination), while detections of other N-DBPs were much more sporadic (Table 1). There
223 appeared to be more detections of the *N*-nitrosamines, NDMA and NDBA, from surface water
224 sources than from groundwater sources (17-67% from surface water sources, compared with 0-50%
225 from groundwater sources), although this was partly contributed to by the detections of these *N*-
226 nitrosamines in some raw surface waters.

227 As shown in Table 2, *N*-nitrosamine concentrations were always below 10 ng/L, while the
228 concentrations of other N-DBPs were less than 10 µg/L in most cases. This is comparable to
229 concentrations reported internationally, where *N*-nitrosamine concentrations have been reported up
230 to 6.4 ng/L for individual species (Brisson et al., 2013; Templeton & Chen, 2010), individual HAN
231 concentrations up to 8 µg/L (Bond et al., 2015; Chu et al., 2011; Goslan et al., 2014; Weinberg et
232 al., 2002), individual HNM concentrations up to 4 µg/L (Bond et al., 2015; Chu et al., 2011;
233 Goslan et al., 2014; Weinberg et al., 2002) and individual HAAs up to 6 µg/L (Bond et al., 2015;
234 Chu et al., 2011; Weinberg et al., 2002). However, a significant concentration of DBAN (maximum

235 26.6 µg/L) was observed in post-chlorination water at site GW4, which also had the highest
236 bromide concentration in its pre-disinfection water. To our knowledge, this is the highest reported
237 concentration of DBAN in drinking waters around the world. While there is currently no guideline
238 in Australia for DBAN, this concentration exceeds the United States federal drinking water
239 guideline for this N-DBP (20 µg/L), but is below the WHO guideline limit (70 µg/L). Similarly, a
240 predominance of brominated HANs (DBAN and BCAN) was previously reported in Australia
241 (Simpson & Hayes, 1998), which was believed to be associated with high DOC and bromide levels
242 in the source waters. In relation to the Australian Drinking Water Guidelines, measured NDMA
243 concentrations in this work were always below the ADWG value of 100 ng/L. While NDBA has
244 been less frequently reported than NDMA in drinking waters, in our survey, NDBA was detected
245 more frequently and at higher concentrations than NDMA in the chlorinated systems (up to 9.4
246 ng/L NDBA). This is higher than the few reported concentrations of NDBA in chlorinated drinking
247 waters in China (up to 3.4 ng/L) (Luo et al., 2012; Wang et al., 2011) and in the United Kingdom
248 (up to 6.4 ng/L) (Templeton & Chen, 2010). NDBA has also been reported at 11 ng/L from a
249 surface water treatment plant in Italy after disinfection with ozone and chlorine dioxide (Pozzi et
250 al., 2011). While a variety of precursors for NDMA have been identified in the literature, the
251 sources of precursors for other *N*-nitrosamines such as NDBA in drinking water systems are not so
252 well known. Rubber products have been reported to be a common source of various *N*-nitrosamines
253 and their precursors, including NDBA (Pensabene et al., 1995; Thompson et al., 1984), and rubber
254 materials used in drinking water pipelines have been implicated in the formation of *N*-nitrosamines
255 in drinking water distribution systems (Morran et al., 2011). In our study, all raw waters were
256 sampled from sampling ports at the water treatment plants, therefore it is possible that contact with
257 rubber components used within the system pipelines may be a source of *N*-nitrosamines in the
258 water. In addition, we note that concentrations of NDBA were higher in surface waters than the
259 groundwaters in this study (Table 2), which suggests that NDBA precursors may be related to
260 NOM found in surface waters, such as algal organic matter. NDBA is known to be a bladder
261 carcinogen in rodents, and even though it is not regulated, it is estimated to have a lower
262 concentration (6 ng/L) for cancer risk (based on 1 in a million lifetime cancer risk according to
263 USEPA Integrated Risk Information System) than NDMA (risk concentration of 10 ng/L).

264 *Relationships with Pre-disinfection Water Characteristics*

265 The molar concentrations of N-DBPs in post-chlorination waters (n=9) were analysed for
266 relationships with pre-disinfection water characteristics (ESM, Table S3) by calculation of
267 Spearman's rank correlation coefficients (SPSS Statistics v20) (ESM, Table S4). The Spearman's
268 correlation method was used as concentrations of N-DBPs were not normally distributed (as tested

269 by calculation of the Kolmogorov-Smirnov Statistic and the Shapiro-Wilk Statistic). For samples
270 where the N-DBP was not detected, a value of zero was allocated.

271 No significant relationships were identified between N-DBPs and the organic nitrogen
272 concentration (OrgN) of pre-disinfection waters, which may be partly due to the lack of N-DBPs in
273 many of the chlorinated systems, and the limited number of sample sites. Although OrgN has been
274 linked to yields of some N-DBPs during bench-scale chlorination or chloramination at high doses
275 (Chu et al., 2010b; Hu et al., 2010; Lee et al., 2007), in our study, the limited detections of N-DBPs
276 under real water treatment conditions may be insufficient to indicate any relationships with OrgN,
277 particularly since OrgN concentrations can be 10-100 times higher than N-DBP concentrations. In
278 addition, OrgN concentrations may not be sufficiently precise since they are prone to compounded
279 errors when determined by the subtraction of inorganic nitrogen (nitrate, nitrite, ammonia) from
280 total dissolved nitrogen, especially in waters where inorganic nitrogen concentrations are high. The
281 majority of pre-disinfection waters (6 of 9) in this study contained more than 50% of inorganic
282 nitrogen, and typically less than 0.1 mg/L-N of OrgN (Table S3).

283 A positive correlation was found between total HANs and DOC concentrations ($\rho=0.887$), which
284 was significant at the 99% level ($p<0.01$). This indicates that the precursors for HANs are related to
285 a fraction of DOC that is poorly removed through conventional treatment and which leads to HAN
286 formation upon chlorination. A significant correlation was also observed between HANs and
287 ammonia ($\text{NH}_3\text{-N}$) ($\rho=0.851$, $p<0.01$). Chlorination of ammonia may also lead to some formation
288 of monochloramine, which may also lead to HAN formation through formation pathways
289 alternative to that of free chlorine (Huang et al., 2012; Shah & Mitch, 2012). Laboratory formation
290 studies have shown that monochloramine can act as the source of nitrogen in DCAN formation,
291 though the yield and extent of nitrogen incorporation of monochloramine into DCAN cannot be
292 easily predicted and varies for different organic precursors and chloramine exposures (Huang et al.,
293 2012; Yang et al., 2012). Thus, it is possible that the increased HAN formation observed in the
294 current study in waters with higher ammonia content may be attributed to the formation of some
295 monochloramine, but controlled laboratory studies would be required to confirm this. There were
296 no correlations observed between the concentrations of the other N-DBPs (HNMs, HAAs, and *N*-
297 nitrosamines), and the pre-disinfection water parameters (Table S3), due to the limited detections of
298 these other N-DBPs in the chlorinated waters.

299 The highest concentration of total N-DBPs was detected at site GW4, representing the elevated
300 concentration of brominated HANs (DBAN and BCAN) formed. It is worth noting that this sample
301 site also had the highest DOC (5.9 mg/L), bromide (1320 $\mu\text{g/L}$) and ammonia (350 $\mu\text{g/L-N}$)
302 concentrations among the pre-disinfection waters, suggesting that these conditions (individually or

303 combined) favour the formation of high concentrations of brominated N-DBPs upon disinfection. In
304 particular, the bromide concentration in the pre-disinfection water at GW4 was at least 3 times
305 higher than in the other groundwater sites (210-350 $\mu\text{g/L}$, ESM Table S3). Several studies have
306 shown that increasing initial bromide concentrations can lead to higher concentrations of
307 brominated DBPs such as THMs, upon disinfection in controlled laboratory experiments (Bond et
308 al., 2014; Bougeard et al., 2010; Hua et al., 2006). Most studies have reported increasing molar
309 yields of THMs with initial bromide concentrations, but this effect has not been consistent for
310 HAAs (Bond et al., 2014; Cowman & Singer, 1996; Hua et al., 2006), and has not yet been reported
311 for N-DBPs. Bond et al. (Bond et al., 2015) recently examined bromine substitution into N-DBPs in
312 drinking water supply systems, and while chloraminated waters demonstrated higher bromine
313 substitution into HANs and HAAs than chlorinated waters, it was not clear whether there was a
314 relationship between initial bromide concentrations and brominated N-DBP concentrations. In our
315 study, there was no clear relationship between bromide in the different pre-disinfection waters and
316 brominated N-DBP concentrations, even when ratios of bromide to DOC or bromide to chlorine
317 dose, were considered. However, the sample set was significantly skewed by the high bromide
318 (1320 $\mu\text{g/L}$) in the GW4 pre-disinfection water (whereas all other sites had $<600 \mu\text{g/L Br}^-$). It is
319 possible that the impact of bromide on N-DBP formation may only become important in waters that
320 exceed a certain threshold concentration of bromide. Furthermore, two other sites (GW1 and SW5)
321 that had relatively high levels of bromide (i.e. 350 $\mu\text{g/L Br}^-$ in GW1 and 550 $\mu\text{g/L Br}^-$ in SW5), but
322 the lowest DOCs (both $<1 \text{ mg/L DOC}$), exhibited the lowest concentrations of N-DBPs after
323 chlorination. This suggests that N-DBP formation will be limited by low DOC concentrations, even
324 in the presence of high bromide concentrations. This effect has been previously observed for HAA
325 formation, as reported by Bond et al. (Bond et al., 2014), where HAA formation was independent of
326 bromide and chlorine dose at low DOC concentrations (1 mg/L), during chlorination of raw waters.
327 Further investigation would be required to understand the effect of bromide on N-DBP formation in
328 different pre-disinfection waters.

329 Spearman's correlation coefficients were also determined between concentrations of different N-
330 DBP species in all post-chlorination waters (ESM, Table S5). There appeared to be moderate
331 correlations between DBAN and DBAAM concentrations ($\rho=0.575$, $p<0.05$), and between
332 dihalogenated HANs (sum of DBAN, DCAN and BCAN) and dihalogenated HAAs (sum of
333 DCAAM and DBAAM) ($\rho=0.545$, $p<0.05$), but no correlation between DCAN and DCAAM
334 concentrations, as there were too few detections of DCAAM in the waters. These findings are in
335 agreement with those in English water supply systems (Bond et al., 2015), that showed a
336 relationship between dihalogenated HANs and HAAs, believed to be associated with the
337 formation of HAAs from hydrolysis of the corresponding HANs (Reckhow et al., 2001). There

338 was also a moderate negative correlation between HNMs and HANs ($\rho=-0.554$, $p<0.05$), and no
339 correlations were observed between *N*-nitrosamines and other N-DBPs.

340 *Formation in the Distribution System*

341 The formation of DBPs can vary quite significantly with residence time or distance in the
342 distribution system (Rodriguez et al., 2007; Shanks et al., 2013). While some DBPs continue to
343 form with time, others may degrade and/or form other DBPs. The variation of N-DBPs in post-
344 chlorination and distribution system waters within each chlorinated system are presented in Figure
345 3. Concentrations of HANs either stayed the same or increased in the distribution for all sample
346 sites except for GW4, while concentrations of other N-DBPs did not follow consistent trends. For
347 GW4, much lower concentrations of HANs were observed in the distribution system water than in
348 the post-chlorination water. In the presence of free chlorine, HANs can degrade and form the
349 corresponding HAAs, which are in turn degraded into HAAs (Reckhow et al., 2001). However,
350 there were no discernible trends between the change in free chlorine residuals and the change in
351 HAN or HAAM concentrations, from post-chlorination to the distribution system. This seemed to
352 suggest that other site-specific factors, such as residence time or temperature, may have affected the
353 formation of HANs and HAAs in the system of site GW4. In the case of *N*-nitrosamines, the
354 significant increase in concentrations observed on two occasions in the distribution system of site
355 SW4 is consistent with findings of previous studies reporting higher concentrations of *N*-
356 nitrosamines with increasing distance from the water treatment plant (Charrois et al., 2004; Charrois
357 et al., 2007; Goslan et al., 2009; Zhao et al., 2006). This was not observed in most of the other
358 sample sites, which may be due in part to the relatively lower concentrations of *N*-nitrosamines in
359 these cases.

360

361 N-DBPs in the Goldfields and Agricultural Water Supply Scheme (GAWSS)

362 *N-DBP Occurrence and Comparison to Chlorinated Systems*

363 Table 3 presents the occurrence of N-DBPs that were detected at least once in the GAWSS within
364 the main pipeline and extensions. Only 4 of the 6 HANs were detected in the GAWSS, and at much
365 lower concentrations than in the chlorinated waters, which is in agreement with laboratory
366 formation studies that have found lower concentrations of HANs from chloramination than from
367 chlorination (Bougeard et al., 2010; Hua & Reckhow, 2007). However, it should also be noted that
368 the raw water for the GAWSS had a relatively low concentration of DOC (2.1 mg/L) (Table S3),
369 which was lower than the DOC of most of the pre-disinfection waters (6 out of 9) from the
370 chlorinated systems. Given the correlation of DOC with HAN concentrations observed in this study,

371 the relatively low DOC of GAWSS raw water could also be a limiting factor for HAN formation.
372 To investigate this possibility, HAN concentrations were normalised by the DOC concentration of
373 either the raw or pre-disinfection waters. While normalisation meant that concentrations between
374 GAWSS and chlorinated systems were more similar, overall the normalised HAN concentration in
375 the GAWSS (median concentration of 0.6 µg/mg C) was still lower than in the chlorinated samples
376 (median concentration of 1.8 µg/mg C). This suggests that the type of disinfectant still has a more
377 significant impact on HAN formation than the DOC concentration.

378 One higher-order halogenated nitrile (2,2-DCPN) was also detected in 2 GAWSS samples, just
379 above the detection limit (0.01 µg/L), consistent with its previously reported detection in a
380 chloraminated distributed water at only 8 ng/L (Kristiana et al., 2012). In contrast, HAAMs were
381 more frequently detected in the GAWSS than in the chlorinated waters. For example, DCAAm and
382 DBAAM were detected in all GAWSS samples (100% detection), and at higher concentrations than
383 in chlorinated waters (i.e. up to 1.9 µg/L DCAAm and 6.3 µg/L DBAAM in GAWSS waters,
384 compared to 0.6 µg/L DCAAm and 1.7 µg/L DBAAM in chlorinated waters). It is well known that
385 HAAMs are formed from the hydrolysis of the corresponding HANs in the presence of free chlorine
386 (Chu et al., 2010a; Reckhow et al., 2001). However, recent work by Huang et al (2012) suggests
387 that HAAMs also form independently during chloramination, and formation of DCAAm was
388 favoured over DCAN during chloramination of a range of waters and natural organic matter types.
389 This supports the current observations that while HANs are higher in the chlorinated systems,
390 HAAMs can form in higher concentrations (than HANs) in the chloraminated system. There were
391 no significant differences in the concentrations of HNMs between chlorinated systems and the
392 chloraminated GAWSS, and HNM concentrations were minimal in both cases (<2 µg/L). However,
393 there were slight differences in terms of N-DBP speciation, where chloropicrin and TCAAm were
394 detected in GAWSS samples, but not in chlorinated samples.

395 As expected, the *N*-nitrosamine NDMA occurred more frequently, and at higher concentrations in
396 the chloraminated GAWSS than in chlorinated waters. NDMA was always detected (100%) in
397 GAWSS samples, at a higher median and maximum concentration (Table 3) than in the chlorinated
398 systems (Table 2), but still well below the ADWG of 100 ng/L. While the median NDMA
399 concentrations in GAWSS (6.6 ng/L and 7.7 ng/L in the main pipeline and the extensions,
400 respectively) were not significantly high (i.e. below 10 ng/L), they fall within the top 30% of
401 concentrations in chloraminated waters from 38 Australian drinking water supplies, as we have
402 recently reported (Liew et al., 2015). There were also more detections of other *N*-nitrosamine
403 species in the GAWSS than in the chlorinated waters, although the concentrations of NDBA were
404 slightly lower in the GAWSS than in the chlorinated surface water sites.

405 As shown in Figure 2, the concentration distributions of different N-DBP classes were different in
406 the chloraminated GAWSS compared to the chlorinated waters . The Mann–Whitney *U* test, the
407 non-parametric equivalent of the student’s t-test, was performed to determine differences in N-DBP
408 concentrations between the chlorinated systems and the chloraminated GAWSS, and confirmed that
409 there were statistically significant differences ($p < 0.01$) for the concentrations of HANs, HAAs
410 and *N*-nitrosamines between chlorinated systems and the GAWSS.

411

412 *Variations in the GAWSS Distribution System*

413 Within the GAWSS, the extension pipelines were considered to be less “well-controlled” compared
414 to the main pipeline, as they were more remote and had longer residence times, which often led to
415 poorer water quality, including nitrification. Comparison of the occurrence of N-DBPs between the
416 GAWSS main pipeline and the extension pipelines (Table 3) show comparable concentrations for 5
417 halonitriles, DCNM, TCAAm and NDMA. However, the extension pipelines exhibited slightly
418 higher median and maximum concentrations of other N-DBPs than the main pipeline. Specifically,
419 there were higher concentrations of 2 HAAs (DBAAm, DCAAm) and 4 *N*-nitrosamines (NDPA,
420 NDBA, NMOR and NPYR), suggesting that the conditions within the extensions could enhance the
421 formation of some of these N-DBPs. Nitrification has been shown to enhance the concentrations of
422 *N*-nitrosamines and other halogenated DBPs (including NDMA, DCAN and DCAAm) in storage
423 facilities within chloraminated distribution systems, where nitrifying biofilms may contribute DBP
424 precursors (Zeng & Mitch, 2016). Along the GAWSS distribution system, there is a section of
425 extension C (Figure 1) that has historically exhibited evidence of nitrification, as characterised by
426 low chloramine residual, low ammonia concentrations, and elevated concentrations of nitrite and
427 nitrate. In this study, the sample point within the nitrification front exhibited higher concentrations
428 of DBAAm (6.3 µg/L), DCAAm (1.9 µg/L), NDBA (3.9 ng/L) and NDPA (1.0 ng/L), higher than
429 any other sample measured within the GAWSS distribution system. The concentration of NDMA
430 (8.3 ng/L) was the highest measured in any of the samples taken within the extension pipelines.
431 However, overall concentrations of HANs were low (≤ 0.5 µg/L). While nitrification appears to
432 enhance the concentrations of some N-DBPs, at the same time, formation may also be influenced by
433 other conditions in the distribution system, such as residual chloramine and temperature.

434 The concentrations of N-DBPs were also assessed along the main GAWSS pipeline, to determine
435 trends in N-DBP formation with increasing distance, as well as with redosing of disinfectant in this
436 long distribution system. Variations in N-DBPs within the extensions were not evaluated to this
437 extent due to the different complex environments and the fewer number of sampling points within
438 each extension. As shown in Figure 4, the concentrations of HANs and HAAs changed

439 significantly with distance along the main pipeline (A to F). All the detected HANs followed a
440 similar trend, forming quickly after the initial chloramination point (at location A), subsequently
441 decreasing, and then increasing again (after rechloramination at location D, and breakpoint
442 chlorination at E) until the far end of the distribution system. In contrast, the DHAAs (DBAAs
443 and DCAAs) seemed to follow a different trend, increasing steadily and subsequently decreasing
444 towards the end of the distribution system. TCAA appeared to increase towards the end of the
445 distribution system, but concentrations were very low ($<0.1 \mu\text{g/L}$) compared to DBAAs and
446 DCAAs. Field measurements of disinfectant residual indicated that the water in the main pipeline
447 was mostly chloraminated, until breakpoint chlorination towards the end of the distribution system
448 at location E. The previous evidence supporting the formation of DCAAs over DCAN with
449 chloramination (Huang et al., 2012) and the degradation of both HANs and HAAs with free
450 chlorine (Reckhow et al., 2001) may explain the predominance of HAAs over HANs in the initial
451 portion of the pipeline (locations A to D), and the converse towards the end of the pipeline (E & F),
452 where HAAs formed initially may have degraded into HANs. Another possible factor affecting
453 the occurrence of HAAs and HANs through the distribution system is the temperature. The
454 temperature of waters through the pipeline varied from 24-34°C (Figure 4), where the highest
455 temperatures were observed around the middle of the pipeline (locations C & D). HANs may have
456 been degraded at the higher temperatures, while the formation of HAAs may have been enhanced.
457 Further analysis of the data with temperatures across all the GAWSS samples ($n=14$) revealed that
458 there were significant correlations in DBAAs and DCAAs concentrations with temperature
459 ($\rho=0.725$ and 0.690 , respectively, $p<0.01$), but correlations with temperature were not significant in
460 the case of HANs. It is possible to conclude that increasing temperatures in the distribution system
461 during chloramination could increase the formation of HAAs. There were no clear trends
462 observed for *N*-nitrosamines or HNMs across the GAWSS distribution system.

463 **Conclusions**

464 This work provides the most comprehensive evaluation of N-DBP concentrations in drinking waters
465 in Australia to date. Various N-DBPs were detected in Western Australian drinking waters from
466 low ng/L (for *N*-nitrosamines) to low $\mu\text{g/L}$ (for other N-DBP classes) concentrations, comparable to
467 typical occurrences elsewhere in the world. However, DBAN was recorded at an elevated
468 concentration ($26.6 \mu\text{g/L}$) in one chlorinated drinking water, which is its highest concentration
469 reported in drinking water to-date. Another interesting finding was of the *N*-nitrosamine, NDBA,
470 which was detected more frequently and at higher concentrations than the more commonly studied
471 NDMA, in the chlorinated systems. The use of chlorine versus chloramine disinfection was found
472 to influence the concentrations and speciation of N-DBPs formed. Dihalogenated HANs were the

473 most dominant N-DBP species found in chlorinated waters, but slightly different concentration
474 distributions were observed in the chloraminated GAWSS. *N*-Nitrosamines and HAAs were more
475 prevalent in the GAWSS than in the chlorinated systems.

476 Although N-DBPs typically occur at concentrations lower than those of the regulated THMs and
477 HAAs, it is important to consider that most of these N-DBPs are not yet regulated, and the health
478 significance of these occurrences requires further investigation. In our study, DCAN, DBAN and
479 NDMA were all found below their existing guideline values (WHO and ADWG). Other
480 unregulated N-DBPs (such as BCAN, NDBA, DBAAm and DCAAm) were also frequently
481 detected, suggesting that these compounds could be considered for further investigation, in addition
482 to the commonly studied N-DBPs.

483 Formation of HANs was correlated to DOC and NH₃-N in the pre-disinfection water, but there
484 were no clear relationships between N-DBPs and other components of nitrogen in the pre-
485 disinfection waters. The high concentrations of brominated N-DBPs (i.e. DBAN) produced at one
486 of the groundwater sites (GW4) that contained high DOC, bromide and ammonia in the pre-
487 disinfection water, implied that these parameters, alone or combined, could influence the formation
488 of brominated N-DBPs; however, low DOC of the pre-disinfection waters can limit the formation of
489 N-DBPs, even in the presence of high bromide. More research is required to assess the relationships
490 between N-DBP formation, bromide and DOC. This study also demonstrates for the first time
491 factors influencing N-DBP occurrence and formation in a large distribution system. Concentrations
492 of N-DBPs can vary significantly with distance in the distribution system, as shown by HAN and
493 HAAs concentrations in the GAWSS, attributable to continuous formation, or degradation into
494 other compounds by free chlorine. Varying temperatures through the distribution system can also
495 influence the formation of N-DBPs, particularly HAAs, where the formation of DBAAs and
496 DCAAs increased with temperature in the distribution system.

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504

505 **Table Captions**

506 **Table 1** Detection frequencies of N-DBPs (that were detected at least once) within chlorinated
 507 systems (Groundwater and Surface Water Sites). n = total number of samples; n.d. = not detected.
 508 Method detection limits for each analyte are presented in the ESM (Table S2).

Detections (%)	Groundwater Sites (GW1-GW4)				Surface Water Sites (SW1-SW5)			
	Raw (n=8)	Post-pretreatment (n=4)	Post-chlorination (n=8)	Distribution System (n=8)	Raw (n=6)	Post-pretreatment ^a (n=4)	Post-chlorination (n=6)	Distribution System (n=6)
MCAN	n.d.	n.d.	n.d.	25%	n.d.	n.d.	17%	17%
MBAN	n.d.	25%	63%	50%	n.d.	n.d.	17%	17%
BCAN	n.d.	75%	88%	100%	n.d.	n.d.	83%	83%
DBAN	n.d.	75%	88%	100%	n.d.	n.d.	83%	100%
DCAN	n.d.	75%	88%	88%	n.d.	n.d.	83%	83%
TCAN	n.d.	n.d.	13%	n.d.	n.d.	n.d.	50%	50%
BCNM	n.d.	n.d.	25%	n.d.	n.d.	n.d.	n.d.	n.d.
DCNM	n.d.	n.d.	38%	50%	n.d.	25%	83%	n.d.
CAAm	n.d.	n.d.	13%	13%	n.d.	n.d.	n.d.	n.d.
DBAAm	n.d.	n.d.	63%	63%	n.d.	25%	33%	50%
DCAAm	n.d.	n.d.	25%	38%	n.d.	25%	17%	17%
NDMA	n.d.	n.d.	n.d.	n.d.	33%	25%	33%	17%
NDPA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	33%
NDBA	n.d.	n.d.	13%	38%	50%	50%	67%	67%

509 ^a Calculated based on 4 data points: 2 pre-chlorination samples (SW4 and SW5) and 2 raw waters (SW2 and SW3 do not apply
 510 pretreatment i.e. raw water is followed directly by chlorination). Pre-chlorination sample from SW1 was not taken and was therefore
 511 not considered.

512

513 **Table 2** Concentrations of N-DBPs detected at least once in chlorinated waters (post-chlorination
514 and distribution system samples) from surface water and groundwater sites. n = total number of
515 samples; n.a. = median is not applicable since there are <50% detections; n.d. = not detected.
516 Method detection limits for each analyte are presented in the ESM (Table S2).

517

N-DBPs	Groundwater Sites (n=16)			Surface Water Sites (n=12)		
	Detections (%)	Median conc.	Maximum conc.	Detections (%)	Median conc.	Maximum conc.
<u>Haloacetonitriles (µg/L)</u>						
MCAN	13%	n.a.	0.2	17%	n.a.	0.1
MBAN	56%	0.2	0.8	17%	n.a.	0.4
BCAN	94%	1.5	5.7	83%	0.9	2.1
DBAN	94%	2.2	26.6	92%	1.3	4.4
DCAN	88%	0.7	2.2	83%	0.5	1.3
TCAN	6%	n.a.	0.2	50%	0.1	1.3
<u>Halonitromethanes (µg/L)</u>						
BCNM	13%	n.a.	0.5	0%	n.d.	n.d.
DCNM	44%	n.a.	1.0	67%	0.3	1.4
<u>Haloacetamides (µg/L)</u>						
CAAm	13%	0	9.2	0%	n.d.	n.d.
DBAAm	63%	0.3	2.3	42%	n.a.	1.7
DCAAm	31%	n.a.	0.6	17%	n.a.	0.6
<u>N-nitrosamines (ng/L)</u>						
NDMA	0%	n.d.	n.d.	25%	n.a.	3.6
NDPA	0%	n.d.	n.d.	17%	n.a.	0.8
NDBA	25%	n.a.	0.9	67%	2	9.4

518

519

520 **Table 3** Concentrations of N-DBPs detected in the GAWSS, in samples along the main pipeline
 521 and two extension pipelines. n = total number of samples; n.a. = median is not applicable since
 522 there are <50% detections; n.d. = not detected. Method detection limits for each analyte are
 523 presented in the ESM (Table S2).

N-DBPs	Main pipeline (n=8)			Extensions (n=6)		
	Detections (%)	Median Conc.	Maximum Conc.	Detections (%)	Median Conc.	Maximum Conc.
<u>Halonitriles (µg/L)</u>						
MBAN	63%	0.3	0.5	83%	0.2	0.6
BCAN	88%	0.5	2.1	83%	0.2	2.3
DBAN	88%	0.7	1.8	83%	0.6	2.3
DCAN	63%	0.2	0.8	50%	0.03	0.6
2,2-DCPN	13%	n.a.	0.01	17%	n.a.	0.01
<u>Halonitromethanes (µg/L)</u>						
BCNM	25%	n.a.	0.07	0%	n.d.	n.d.
DCNM	88%	0.09	0.3	100%	0.1	0.2
Chloropicrin	75%	0.05	0.09	67%	0.07	0.1
<u>Haloacetamides (µg/L)</u>						
DBAAm	100%	1.3	3.7	100%	3.4	6.3
DCAAm	100%	0.3	1.1	100%	1.1	1.9
TCAAm	25%	n.a.	0.06	17%	n.a.	0.03
<u>N-Nitrosamines (ng/L)</u>						
NDMA	100%	6.6	9.9	100%	7.7	8.3
NDPA	100%	0.5	0.6	100%	0.7	1.0
NDBA	0%	n.d.	n.d.	50%	1.0	3.9
NMOR	0%	n.d.	n.d.	13%	n.a.	1.0
NPYR	38%	n.a.	0.3	100%	0.3	0.7

524

525 **Figure Captions**

526

527 **Fig. 1** Simplified schematic of sample points (shown in grey circles) located along the GAWSS
528 main pipeline (A to F) and along 2 extension pipelines, showing points of disinfectant addition.
529 Numbers in grey represent approximate water residence times to these points, in days (these are
530 residence times in summer, when sampling occurred). The location of the nitrification front in
531 extension C is also identified. Note: Diagram is not to-scale

532 **Fig. 2** Box plots showing distributions of N-DBP concentrations in waters from chlorinated sites
533 and the chloraminated GAWSS (all post-disinfection and distribution system samples), expressed as
534 total concentrations (sum of all species within each N-DBP class). *N*-Nitrosamine concentrations
535 are on a different scale (ng/L) and therefore shown separately to the other N-DBPs. Points (* and o)
536 lying outside box were identified as outliers and were not considered in the distribution

537 **Fig. 3** Total concentrations of a) HANs, b) HNMs, c) HAAMs, and d) *N*-nitrosamines in post-
538 chlorination and distribution system waters within each chlorinated system. (A) and (B) represent
539 the first and second sampling occasions for sites that were sampled twice

540 **Fig. 4** Variation of the concentrations of (b) HANs and (c) HAAMs with distance along the
541 GAWSS main pipeline (a). Distances are approximate only and represent the distance between
542 locations. Temperatures (a) at each point represent the temperatures of water samples. In (c), left
543 vertical axis represents DBAAM and DCAAM concentrations, and right vertical axis represents
544 TCAAM concentration

545

546

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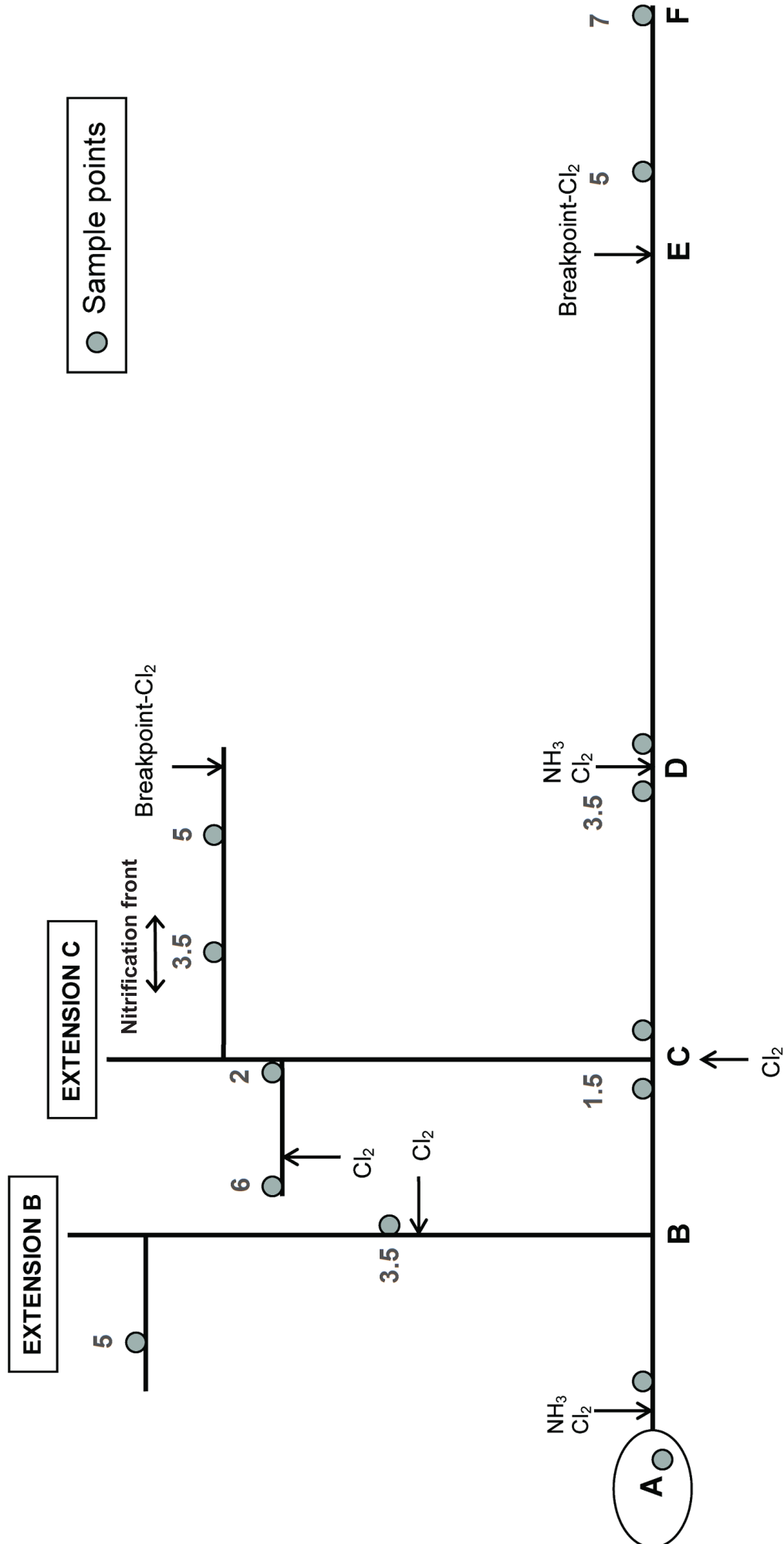
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747

Figure 1 revised



● Sample points

EXTENSION B

EXTENSION C

A

B

C

D

E

F

NH_3
 Cl_2

Cl_2

Cl_2

Nitrification front

Nitrification front

NH_3
 Cl_2

Breakpoint- Cl_2

Breakpoint- Cl_2

● Sample points

Figure 2

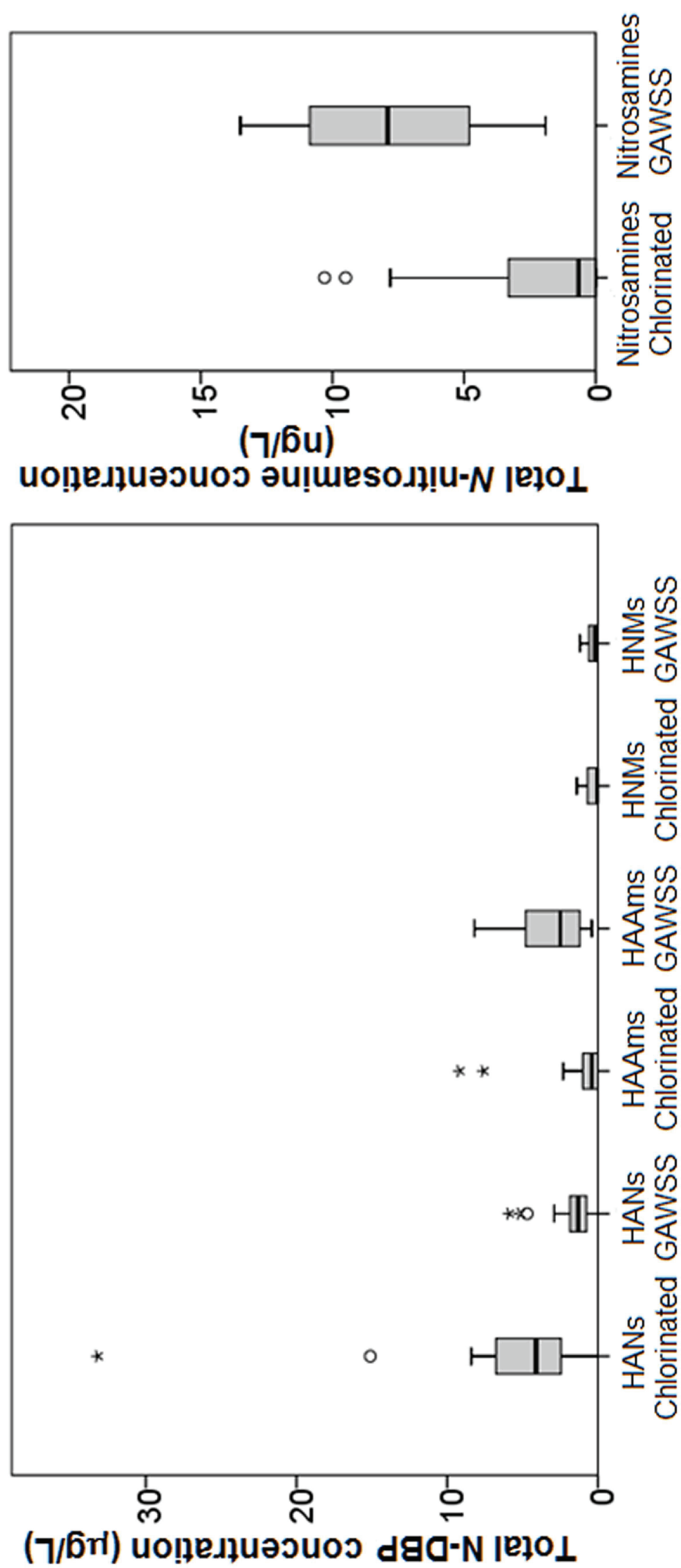


Figure 3

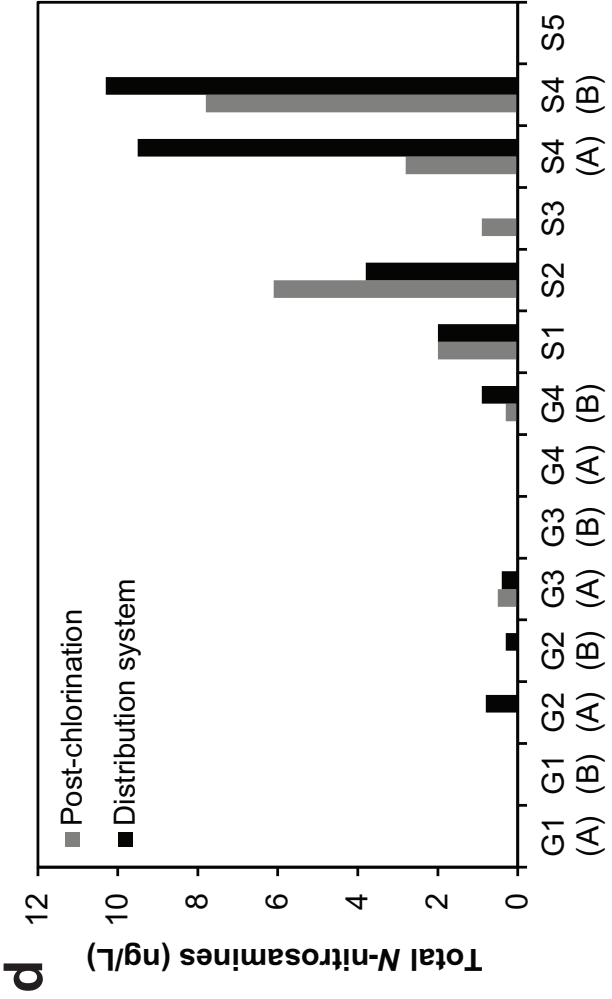
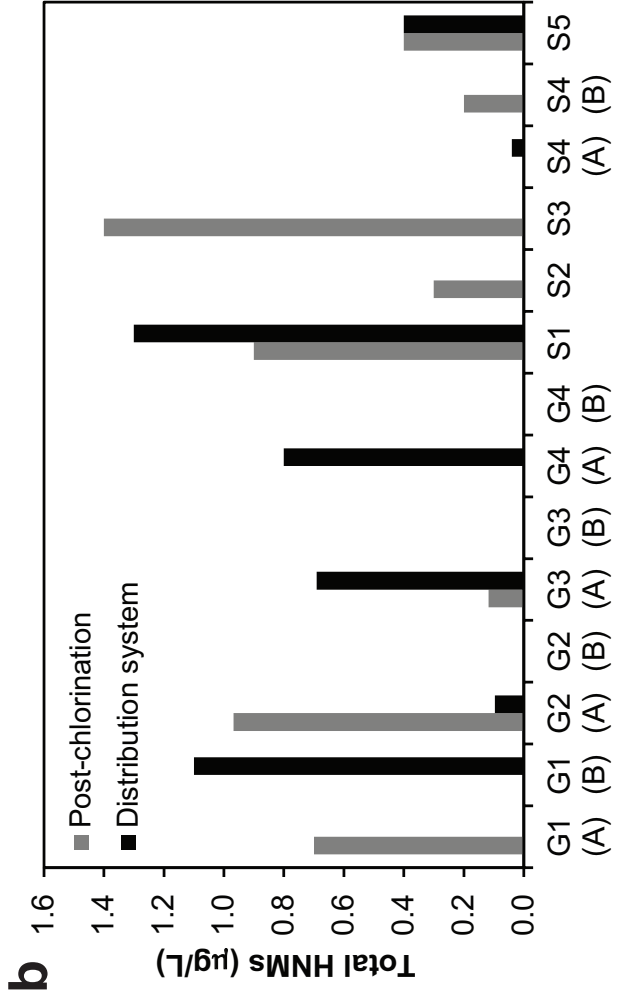
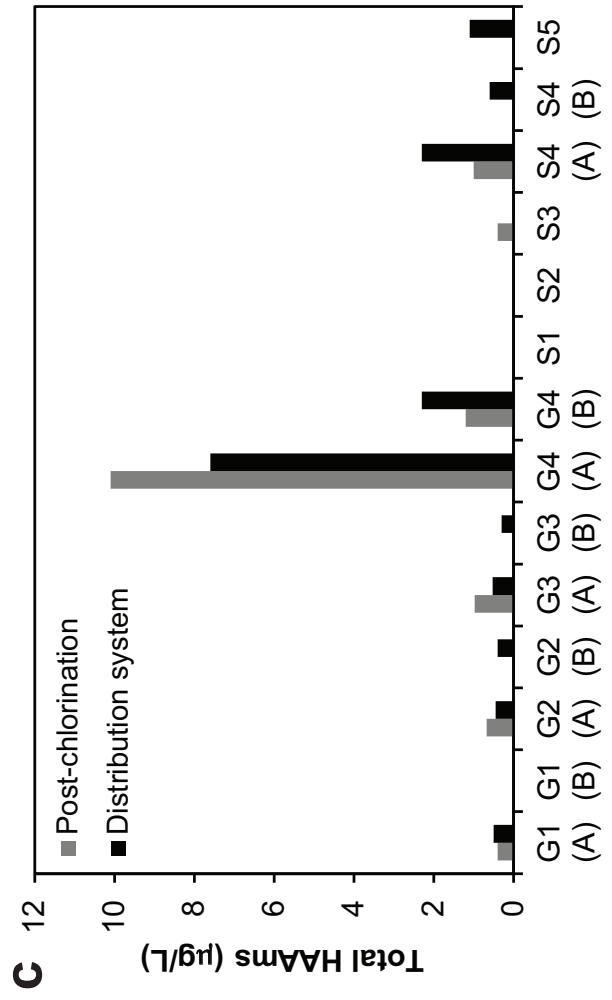
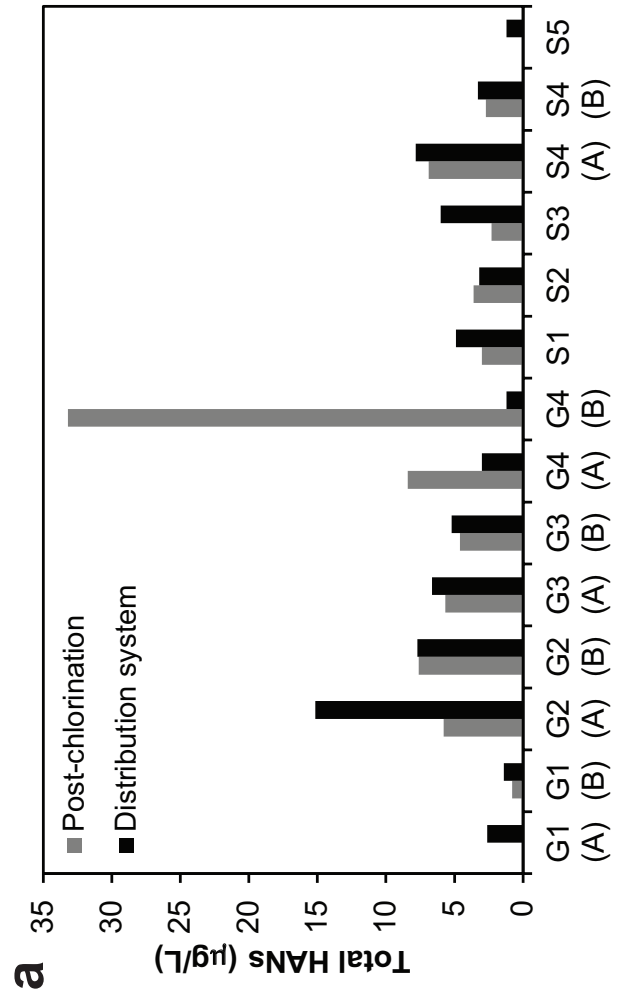


Figure 4

