

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

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Abstract The presence of nitrogenous disinfection by-products (N-DBPs) in drinking water supplies is a public health concern, particularly since some N-DBPs have been reported to be more toxic than the regulated trihalomethanes and haloacetic acids. In this paper, a comprehensive evaluation of the presence of N-DBPs in 10 drinking water supply systems in Western Australia is presented. A suite of 28 N-DBPs, including *N*-nitrosamines, haloacetonitriles (HANs), haloacetamides (HAAs) and halonitromethanes (HNMs), were measured and evaluated for relationships with bulk parameters in the waters before disinfection. A number of N-DBPs were frequently detected in disinfected waters, although at generally low concentrations (<10 ng/L for *N*-nitrosamines and <10 µg/L for other N-DBPs) and below health guideline values where they exist. While there were no clear relationships between N-DBP formation and organic nitrogen in the pre-disinfection water, N-DBP concentrations were significantly correlated with dissolved organic carbon (DOC) and ammonia, and these, in addition to high bromide in one of the waters, led to elevated concentrations of brominated

HANs (26.6 µg/L of dibromoacetonitrile). There were significant differences in the occurrence of all classes of N-DBPs between chlorinated and chloraminated waters, except for HNMs, which were detected at relatively low concentrations in both water types. Trends observed in one large distribution system suggest that N-DBPs can continue to form or degrade within distribution systems, and redosing of disinfectant may cause further by-product formation.

Keywords Nitrogenous disinfection by-products · *N*-Nitrosamines · Haloacetonitriles · Haloacetamides · Chloramination · Distribution system

Introduction

Drinking water disinfection is of utmost importance for water treatment to eliminate waterborne pathogens and prevent transmission of waterborne diseases (Hrudey 2009). However, it results in unintended side effects when disinfectants, such as chlorine or monochloramine, react with natural organic matter (NOM) and/or bromide/iodide to form disinfection by-products (DBPs). Drinking water DBPs have emerged as a public health issue since they have been implicated with adverse health effects in reproduction and cancer (Richardson 2003). Over 600 DBPs have been identified, but only a relatively small proportion has been quantified in drinking waters (Krasner et al. 2006; Richardson et al. 2007). Furthermore, the DBPs identified so far account for less than 50 % of the total organic halides in disinfected drinking

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water (Krasner et al. 2006), indicating that there is still a large percentage of unknown DBPs, which are potentially more toxic than conventional DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs). One particular group of DBPs that have not been extensively studied are nitrogenous DBPs (N-DBPs), which may form from water sources with a high content of dissolved organic nitrogen, especially when impacted by wastewater or algae (Bond et al. 2012; Lee et al. 2007). Major classes of N-DBPs that have been previously identified include the *N*-nitrosamines, haloacetonitriles (HANs), halonitromethanes (HNMs) and haloacetamides (HAAs) (Liew et al. 2012a). Interest in N-DBPs has grown steadily in recent years since they are perceived to be a greater human health risk than the presently regulated THMs and HAAs. For example, *in vitro* toxicological studies have shown that HANs, HNMs and HAAs are much more genotoxic and cytotoxic than the regulated HAAs (Muellner et al. 2007; Plewa et al. 2004, 2008). This has led to the conclusion that N-DBPs are more toxic than non-nitrogenous DBPs. In addition, *N*-nitrosamines, such as *N*-nitrosodimethylamine (NDMA), have become a significant health concern in drinking water supplies due to their high carcinogenic potency (CDPH 2011; IARC 1978). The World Health Organisation (WHO) recommends drinking water guideline values for dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN) and NDMA of 20 µg/L, 70 µg/L and 100 ng/L, respectively. In the United States, federal drinking water guideline levels have been established for DCAN and DBAN, at 6 and 20 µg/L, respectively (USEPA 2007). The latest version of the Australian Drinking Water Guidelines (ADWG) includes guideline values for only one N-DBP (NDMA) at a value of 100 ng/L (NHMRC-NRMMC 2011). Various health guidelines for the presence of NDMA in drinking water have been adopted by agencies in other parts of the world. The California Department of Public Health has advised notification levels of 10 ng/L for NDMA and two other *N*-nitrosamines, with future regulation under consideration (CDPH 2011), while Health Canada has recommended a drinking water guideline of 40 ng/L for NDMA (HealthCanada 2012), and the Drinking Water Inspectorate for England and Wales has set a 'wholesomeness limit' of 10 ng/L for NDMA (DWI 2008).

The typical concentrations of N-DBPs identified in drinking waters have been previously reviewed (Bond et al. 2011; Liew et al. 2012a). The *N*-nitrosamines

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

Studies dating back to the 1970s have shown that HANs are nearly ubiquitous in chlorinated drinking waters, with the dihalogenated species being the most prevalent (Krasner et al. 1989; Krasner et al. 2006; Liew et al. 2012a; Oliver 1983; Williams et al. 1997). Concentrations of DCAN, DBAN and bromochloroacetonitrile (BCAN) in drinking waters are generally below 10 µg/L (Goslan et al. 2009; Krasner et al. 1989; Williams et al. 1997), but concentrations as high as 41 µg/L have been recorded during the U.S. EPA Information Collection Rule, for the sum of 4 HANs, DCAN, DBAN, BCAN and trichloroacetonitrile (TCAN) (McGuire et al. 2002). Concentrations of HNMs in drinking waters are typically lower than the HANs and are mostly below 5 µg/L (Simpson and Hayes 1998; Weinberg et al. 2002; Williams et al. 1997), but have been shown to increase when ozonation is applied before chlorine or chloramine treatment (Hoigné and Bader 1988; Krasner et al. 2006; Weinberg et al. 2002). Haloacetamides have been reported at low microgram per litre concentrations (<10 µg/L) in chlorinated and chloraminated drinking waters (Krasner et al. 2006; Weinberg et al. 2002). Like the HANs, the dihalogenated species, particularly dichloroacetamide (DCAAm), have been found to be the major HAAs species (Chu et al. 2012; Krasner et al. 2006). The occurrence of these N-DBPs in drinking water distribution systems is complicated by the fact that the presence of residual chlorine can

cause N-DBPs, such as HANs and HAAs, to degrade after initial formation (Reckhow et al. 2001).

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

The aim of this study was to investigate the formation and occurrence of a suite of 28 N-DBPs, including haloacetonitriles (HANs), halonitromethanes (HNMs), haloacetamides (HAAs) and the non-halogenated *N*-nitrosamines, in 10 different drinking water systems in Western Australia. This represents the first comprehensive survey of N-DBP occurrence in Australia and one of only a few such studies in the world. Drinking water treatment supply schemes were selected for sampling based on factors predicted to influence the formation of N-DBPs, such as their use of nitrogen-containing treatment polymers (e.g. polyacrylamide) and/or ion exchange resins during treatment, and the organic nitrogen content and/or dissolved organic carbon (DOC) content in their source waters. The majority of drinking water systems in Western Australia utilise chlorine disinfection, but extensive sampling was also undertaken throughout the Goldfields and Agricultural Water Supply Scheme (GAWSS), which is Western Australia's only chloraminated water supply and spans over several thousand kilometres of distribution pipeline in total. Occurrence data was used to (1) identify the most frequently occurring and most abundant N-DBPs, (2) examine relationships between N-DBP formation and bulk water parameters, (3) compare N-DBPs in chlorinated and chloraminated systems, and (4) examine changes in N-DBPs in an extensive chloraminated distribution system.

Methodology

Sampling locations

Sample sites included four groundwater treatment plants utilising chlorination for disinfection in metropolitan Perth (GW1-GW4), five surface water treatment plants using chlorination in regional Western Australia (SW1-SW5) and one drinking water treatment plant and distribution system using chloramination (with monochloramine and chlorine addition along the distribution system) in regional Western Australia (GAWSS). Site descriptions and factors of interest for selected sample sites are presented in the Electronic supplementary material (ESM) (Table S1). Sampling occurred between June 2010 and May 2012. Each site was typically sampled at the raw water stage, post-disinfection (at the treatment plant outlet), and in the distribution system. Some chlorinated sites performed treatment for NOM removal (e.g. coagulation/flocculation followed by filtration) prior to chlorination. At a later stage in the survey, samples after these initial treatment steps (denoted 'post-pretreatment' samples in this work, i.e. after NOM removal processes) were also included to provide better representation of the water quality just before disinfection. Therefore, some of the sample sites (GW1, GW2, GW3, GW4 and SW4) were sampled on two occasions to include the post-pretreatment sample point (when not included in the first instance). All dates of sampling are included in ESM Table S1. The GAWSS was sampled more intensively than the chlorinated systems due to the larger size of the distribution network, and a total of 14 points were sampled within this system. Figure 1 shows a schematic diagram of all the samples taken along the main GAWSS pipeline, as well as along two extension pipelines emanating from the main pipeline.

Sample collection

Quenching agents were used in sample bottles to quench disinfectant residuals at the time of sampling and were appropriate for each group of analytes. For *N*-nitrosamines, samples were collected in 1-L amber glass bottles containing ascorbic acid (20 mg/L) for quenching. For HANs, samples were collected in 60-mL clear vials containing 1 g of solid mixture [of ascorbic acid (0.24 g), KH_2PO_4 (198 g) and Na_2HPO_4 (2.0 g)]. For HNMs and HAAs, samples were collected in 60-mL

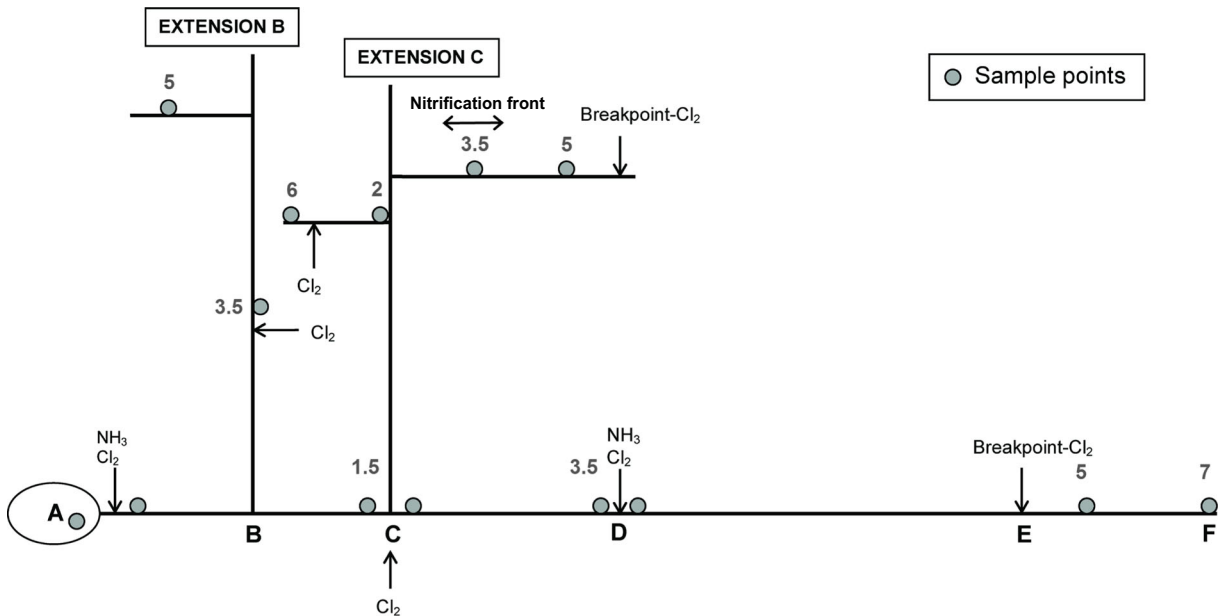


Fig. 1 Simplified schematic of sample points (shown in grey circles) located along the GAWSS main pipeline (A to F) and along two extension pipelines, showing points of disinfectant addition. Numbers in grey represent approximate water residence

times to these points, in days (these are residence times in summer, when sampling occurred). The location of the nitrification front in extension C is also identified. Note: Diagram is not to scale

clear vials containing ammonium chloride (100 mg/L). We have previously recommended the use of ammonium chloride as a quenching agent for HNMs and HAAs (Liew et al. 2012b), owing to decomposition of brominated HNMs during application of other quenching agents. Note that ammonium chloride is a quenching agent specifically for chlorine, as it converts a free chlorine residual to chloramines (Kristiana et al. 2014). In the case of chloramination, the chloramine residual is not quenched per se, but rather the decrease in Cl_2/N ratio of the water has been shown to lower DBP formation (Chu et al. 2013). Single samples were analysed as soon as possible to minimise analyte degradation. For DOC, samples were collected in 40-mL clear vials containing sodium sulphite (25 mg/L). For other water quality parameters, samples for bromide and iodide were collected in 50-mL plastic bottles containing sodium sulphite (25 mg/L), while samples for nitrogen composition (ammonia, nitrate, nitrite, total nitrogen) were collected in 100-mL plastic bottles.

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

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

Water quality parameters of samples

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

Analyses of N-DBPs

A total of 28 N-DBPs were measured. This included eight halogenated nitriles [dibromoacetonitrile (DBAN),

dichloroacetonitrile (DCAN), chloroacetonitrile (MCAN), trichloroacetonitrile (TCAN), bromoacetonitrile (MBAN), bromochloroacetonitrile (BCAN), 2,2-dichloropropanenitrile and 2,2-dibromobutanenitrile], seven HNMs [trichloronitromethane (chloropicrin), tribromonitromethane (bromopicrin), dichloronitromethane (DCNM), dibromonitromethane (DBNM), bromochloronitromethane (BCNM), bromodichloronitromethane (BDCNM), dibromochloronitromethane (DBCNM)], five HAAs [chloroacetamide (CAAm), bromoacetamide (BAAm), dichloroacetamide (DCAAm), dibromoacetamide (DBAAm), trichloroacetamide (TCAAm)] and eight *N*-nitrosamines [*N*-nitrosodimethylamine (NDMA), *N*-nitrosoethylmethylamine (NEMA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosodi-*n*-butylamine (NDBA), *N*-nitrosopiperidine (NPIP), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosomorpholine (NMOR)]. N-DBPs were analysed in three separate analytical methods using gas chromatography-mass spectrometry (GC-MS) following different organic extraction methods for different DBP groups. Halogenated nitriles were analysed using a method described by Kristiana et al. (2012), employing solid-phase microextraction (SPME) followed by GC-MS. HNMs and HAAs were analysed together in a method described by Liew et al. (2012b), using liquid-liquid extraction followed by GC-MS. *N*-Nitrosamines were analysed according to the method of Charrois et al. (2004), with minor modifications, employing solid-phase extraction (SPE) followed by GC-MS operating with ammonia positive chemical ionisation. Method detection limits were determined for every analytical run using triplicate measurements of low concentration standards (USEPA 2005) and are presented in the ESM (Table S2).

Results and discussion

N-DBPs in chlorinated drinking water systems

Water quality and N-DBP occurrence

An overview of pre-disinfection water characteristics in the nine chlorinated systems surveyed is presented in the ESM (Table S3). For those plants that utilised pretreatment for DOC removal, waters were characterised after

pretreatment and just before disinfection, to provide a direct comparison for subsequent N-DBP formation upon disinfection. Thus, 'pre-disinfection water' refers to the raw water (for sites that do not perform any pretreatment before disinfection) or post-pretreatment water (for sites that perform some form of NOM removal before disinfection).

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

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

Table 1 Detection frequencies of N-DBPs (that were detected at least once) within chlorinated systems (groundwater and surface water sites)

Detections (%) N-DBPs	Groundwater sites (GW1–GW4)				Surface water sites (SW1–SW5)			
	Raw (<i>n</i> = 8)	Post-pretreatment (<i>n</i> = 4)	Post-chlorination (<i>n</i> = 8)	Distribution system (<i>n</i> = 8)	Raw (<i>n</i> = 6)	Post-pretreatment ^a (<i>n</i> = 4)	Post-chlorination (<i>n</i> = 6)	Distribution system (<i>n</i> = 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 %

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

Method detection limits for each analyte are presented in the ESM (Table S2)

n total number of samples, *n.d.* not detected

However, a significant concentration of DBAN (maximum 26.6 µg/L) was observed in post-chlorination water at site GW4, which also had the highest bromide concentration in its pre-disinfection water. To our knowledge, this is the highest reported concentration of DBAN in drinking waters around the world. While there is currently no guideline in Australia for DBAN, this concentration exceeds the United States federal drinking water guideline for this N-DBP (20 µg/L), but is below the WHO guideline limit (70 µg/L). Similarly, a predominance of brominated HANs (DBAN and BCAN) was previously reported in Australia (Simpson and Hayes 1998), which was believed to be associated with high DOC and bromide levels in the source waters. In relation to the Australian Drinking Water Guidelines, measured NDMA concentrations in this work were always below the ADWG value of 100 ng/L. While NDBA has been less frequently reported than NDMA in drinking waters, in our survey, NDBA was detected more frequently and at higher concentrations than NDMA in the chlorinated systems (up to 9.4 ng/L NDBA). This is higher than the few

reported concentrations of NDBA in chlorinated drinking waters in China (up to 3.4 ng/L) (Luo et al. 2012; Wang et al. 2011) and in the United Kingdom (up to 6.4 ng/L) (Templeton and Chen 2010). NDBA has also been reported at 11 ng/L from a surface water treatment plant in Italy after disinfection with ozone and chlorine dioxide (Pozzi et al. 2011). While a variety of precursors for NDMA have been identified in the literature, the sources of precursors for other *N*-nitrosamines such as NDBA in drinking water systems are not so well known. Rubber products have been reported to be a common source of various *N*-nitrosamines and their precursors, including NDBA (Pensabene et al. 1995; Thompson et al. 1984), and rubber materials used in drinking water pipelines have been implicated in the formation of *N*-nitrosamines in drinking water distribution systems (Morran et al. 2011). In our study, all raw waters were sampled from sampling ports at the water treatment plants; therefore, it is possible that contact with rubber components used within the system pipelines may be a source of *N*-nitrosamines in the water. In addition, we note that concentrations of NDBA were higher in

Table 2 Concentrations of N-DBPs detected at least once in chlorinated waters (post-chlorination and distribution system samples) from surface water and groundwater sites

N-DBPs	Groundwater sites (n = 16)			Surface water sites (n = 12)		
	Detections (%)	Median concentration	Maximum concentration	Detections (%)	Median concentration	Maximum concentration
Haloacetonitriles (µg/L)						
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
Halonitromethanes (µg/L)						
BCNM	13 %	n.a.	0.5	0 %	n.d.	n.d.
DCNM	44 %	n.a.	1.0	67 %	0.3	1.4
Haloacetamides (µg/L)						
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
N-Nitrosamines (ng/L)						
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

Method detection limits for each analyte are presented in the ESM (Table S2)

n total number of samples, n.a. median is not applicable since there are <50 % detections, n.d. not detected

surface waters than the groundwaters in this study (Table 2), which suggests that NDBA precursors may be related to NOM found in surface waters, such as algal organic matter. NDBA is known to be a bladder carcinogen in rodents, and even though it is not regulated, it is estimated to have a lower concentration (6 ng/L) for cancer risk (based on 1 in a million lifetime cancer risk according to USEPA Integrated Risk Information System) than NDMA (risk concentration of 10 ng/L).

Relationships with pre-disinfection water characteristics

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

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

No significant relationships were identified between N-DBPs and the organic nitrogen concentration (OrgN) of pre-disinfection waters, which may be partly due to the lack of N-DBPs in many of the chlorinated systems and the limited number of sample sites. Although OrgN has been linked to yields of some N-DBPs during bench-scale chlorination or chloramination at high doses (Chu et al. 2010b; Hu et al. 2010; Lee et al. 2007), in our study, the limited detections of N-DBPs under real water treatment conditions may be insufficient to indicate any relationships with OrgN, particularly since OrgN concentrations can be 10–100 times higher than N-DBP concentrations. In addition, OrgN concentrations may not be sufficiently precise since they are prone to compounded errors when determined by the subtraction of inorganic nitrogen (nitrate, nitrite and

ammonia) from total dissolved nitrogen, especially in waters where inorganic nitrogen concentrations are high. The majority of pre-disinfection waters (six of nine) in this study contained more than 50 % of inorganic nitrogen and typically less than 0.1 mg/L-N of OrgN (Table S3).

A positive correlation was found between total HANs and DOC concentrations ($\rho = 0.887$), which was significant at the 99 % level ($p < 0.01$). This indicates that the precursors for HANs are related to a fraction of DOC that is poorly removed through conventional treatment and which leads to HAN formation upon chlorination. A significant correlation was also observed between HANs and ammonia (NH₃-N) ($\rho = 0.851$, $p < 0.01$). Chlorination of ammonia may also lead to some formation of monochloramine, which may also lead to HAN formation through formation pathways alternative to that of free chlorine (Huang et al. 2012; Shah and Mitch 2012). Laboratory formation studies have shown that monochloramine can act as the source of nitrogen in DCAN formation, though the yield and extent of nitrogen incorporation of monochloramine into DCAN cannot be easily predicted and varies for different organic precursors and chloramine exposures (Huang et al. 2012; Yang et al. 2012). Thus, it is possible that the increased HAN formation observed in the current study in waters with higher ammonia content may be attributed to the formation of some monochloramine, but controlled laboratory studies would be required to confirm this. There were no correlations observed between the concentrations of the other N-DBPs (HNMs, HAAs and *N*-nitrosamines), and the pre-disinfection water parameters (Table S3), due to the limited detections of these other N-DBPs in the chlorinated waters.

The highest concentration of total N-DBPs was detected at site GW4, representing the elevated concentration of brominated HANs (DBAN and BCAN) formed. It is worth noting that this sample site also had the highest DOC (5.9 mg/L), bromide (1320 µg/L) and ammonia (350 µg/L-N) concentrations amongst the pre-disinfection waters, suggesting that these conditions (individually or combined) favour the formation of high concentrations of brominated N-DBPs upon disinfection. In particular, the bromide concentration in the pre-disinfection water at GW4 was at least three times higher than in the other groundwater sites (210–350 µg/L, ESM Table S3). Several studies have shown that

increasing initial bromide concentrations can lead to higher concentrations of brominated DBPs, such as THMs, upon disinfection in controlled laboratory experiments (Bond et al. 2014; Bougeard et al. 2010; Hua et al. 2006). Most studies have reported increasing molar yields of THMs with initial bromide concentrations, but this effect has not been consistent for HAAs (Bond et al. 2014; Cowman and Singer 1996; Hua et al. 2006) and has not yet been reported for N-DBPs. Bond et al. (2015) recently examined bromine substitution into N-DBPs in drinking water supply systems, and while chloraminated waters demonstrated higher bromine substitution into HANs and HAAs than chlorinated waters, it was not clear whether there was a relationship between initial bromide concentrations and brominated N-DBP concentrations. In our study, there was no clear relationship between bromide in the different pre-disinfection waters and brominated N-DBP concentrations, even when ratios of bromide to DOC or bromide to chlorine dose were considered. However, the sample set was significantly skewed by the high bromide (1320 µg/L) in the GW4 pre-disinfection water (whereas all other sites had <600 µg/L Br⁻). It is possible that the impact of bromide on N-DBP formation may only become important in waters that exceed a certain threshold concentration of bromide. Furthermore, two other sites (GW1 and SW5) that had relatively high levels of bromide (i.e. 350 µg/L Br⁻ in GW1 and 550 µg/L Br⁻ in SW5), but the lowest DOCs (both <1 mg/L DOC), exhibited the lowest concentrations of N-DBPs after chlorination. This suggests that N-DBP formation will be limited by low DOC concentrations even in the presence of high bromide concentrations. This effect has been previously observed for HAA formation, as reported by Bond et al. (2014), where HAA formation was independent of bromide and chlorine dose at low DOC concentrations (1 mg/L), during chlorination of raw waters. Further investigation would be required to understand the effect of bromide on N-DBP formation in different pre-disinfection waters.

Spearman's correlation coefficients were also determined between concentrations of different N-DBP species in all post-chlorination waters (ESM, Table S5). There appeared to be moderate correlations between DBAN and DBAAM concentrations ($\rho = 0.575$, $p < 0.05$), and between dihalogenated HANs (sum of

DBAN, DCAN and BCAN) and dihalogenated HAAs (sum of DCAAm and DBAAm) ($\rho = 0.545, p < 0.05$), but no correlation between DCAN and DCAAm concentrations as there were too few detections of DCAAm in the waters. These findings are in agreement with those in English water supply systems (Bond et al. 2015) that showed a relationship between dihalogenated HANs and HAAs, believed to be associated with the formation of HAAs from hydrolysis of the corresponding HANs (Reckhow et al. 2001). There was also a moderate negative correlation between HNMs and HANs ($\rho = -0.554, p < 0.05$), and no correlations were observed between *N*-nitrosamines and other N-DBPs.

Formation in the distribution system

The formation of DBPs can vary quite significantly with residence time or distance in the distribution system (Rodriguez et al. 2007; Shanks et al. 2013). While some DBPs continue to form with time, others may degrade and/or form other DBPs. The variation of N-DBPs in post-chlorination and distribution system waters within each chlorinated system are presented in Fig. 2. Concentrations of HANs either stayed the same or increased in the distribution for

all sample sites except for GW4, while concentrations of other N-DBPs did not follow consistent trends. For GW4, much lower concentrations of HANs were observed in the distribution system water than in the post-chlorination water. In the presence of free chlorine, HANs can degrade and form the corresponding HAAs, which are in turn degraded into HAAs (Reckhow et al. 2001). However, there were no discernible trends between the change in free chlorine residuals and the change in HAN or HAAs concentrations, from post-chlorination to the distribution system. This seemed to suggest that other site-specific factors, such as residence time or temperature, may have affected the formation of HANs and HAAs in the system of site GW4. In the case of *N*-nitrosamines, the significant increase in concentrations observed on two occasions in the distribution system of site SW4 is consistent with findings of previous studies reporting higher concentrations of *N*-nitrosamines with increasing distance from the water treatment plant (Charrois et al. 2004, 2007; Goslan et al. 2009; Zhao et al. 2006). This was not observed in most of the other sample sites, which may be due in part to the relatively lower concentrations of *N*-nitrosamines in these cases.

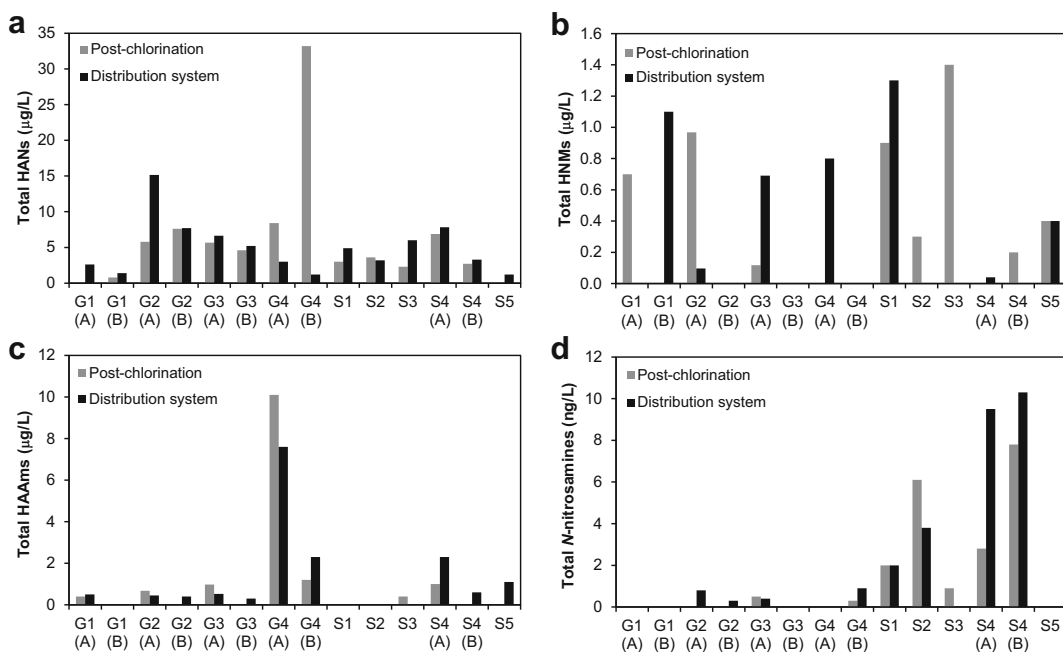


Fig. 2 Total concentrations of **a** HANs, **b** HNMs, **c** HAAs, and **d** *N*-nitrosamines in post-chlorination and distribution system waters within each chlorinated system. (A) and (B) represent the first and second sampling occasions for sites that were sampled twice

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

N-DBP occurrence and comparison to chlorinated systems

Table 3 presents the occurrence of N-DBPs that were detected at least once in the GAWSS within the main pipeline and extensions. Only four of the six HANs were detected in the GAWSS, and at much lower concentrations than in the chlorinated waters, which is in agreement with laboratory formation studies that have found lower concentrations of HANs from chloramination than from chlorination (Bougeard et al. 2010; Hua and Reckhow 2007). However, it should also be noted that the raw water for the GAWSS had a relatively low concentration of DOC (2.1 mg/L) (Table S3), which was lower than the DOC of most of the pre-disinfection waters (six out of nine) from the

chlorinated systems. Given the correlation of DOC with HAN concentrations observed in this study, the relatively low DOC of GAWSS raw water could also be a limiting factor for HAN formation. To investigate this possibility, HAN concentrations were normalised by the DOC concentration of either the raw or pre-disinfection waters. While normalisation meant that concentrations between GAWSS and chlorinated systems were more similar, overall the normalised HAN concentration in the GAWSS (median concentration of 0.6 $\mu\text{g}/\text{mg C}$) was still lower than in the chlorinated samples (median concentration of 1.8 $\mu\text{g}/\text{mg C}$). This suggests that the type of disinfectant still has a more significant impact on HAN formation than the DOC concentration.

One higher-order halogenated nitrile (2,2-DCPN) was also detected in two GAWSS samples, just above the detection limit (0.01 $\mu\text{g}/\text{L}$), consistent with its previously reported detection in a chloraminated distributed water at only 8 ng/L (Kristiana et al. 2012). In contrast,

Table 3 Concentrations of N-DBPs detected in the GAWSS, in samples along the main pipeline and two extension pipelines

N-DBPs	Main pipeline ($n = 8$)			Extensions ($n = 6$)		
	Detections (%)	Median concentration	Maximum concentration	Detections (%)	Median concentration	Maximum concentration
Halonitriles ($\mu\text{g}/\text{L}$)						
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
Halonitromethanes ($\mu\text{g}/\text{L}$)						
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
Haloacetamides ($\mu\text{g}/\text{L}$)						
DBAAm	100 %	1.3	3.7	100 %	3.4	6.3
DCAAm	100 %	0.3	1.1	100 %	1.1	1.9
TCAA	25 %	n.a.	0.06	17 %	n.a.	0.03
<i>N</i> -Nitrosamines (ng/L)						
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

Method detection limits for each analyte are presented in the ESM (Table S2)

n total number of samples, *n.a.* median is not applicable since there are <50 % detections, *n.d.* not detected

HAAs were more frequently detected in the GAWSS than in the chlorinated waters. For example, DCAAm and DBAAm were detected in all GAWSS samples (100 % detection), and at higher concentrations than in chlorinated waters (i.e. up to 1.9 µg/L DCAAm and 6.3 µg/L DBAAm in GAWSS waters, compared to 0.6 µg/L DCAAm and 1.7 µg/L DBAAm in chlorinated waters). It is well known that HAAs are formed from the hydrolysis of the corresponding HANs in the presence of free chlorine (Chu et al. 2010a; Reckhow et al. 2001). However, recent work by Huang et al. (2012) suggests that HAAs also form independently during chloramination, and formation of DCAAm was favoured over DCAN during chloramination of a range of waters and natural organic matter types. This supports the current observations that while HANs are higher in the chlorinated systems, HAAs can form in higher concentrations (than HANs) in the chloraminated system. There were no significant differences in the concentrations of HNMs between chlorinated systems and the chloraminated GAWSS, and HNM concentrations were minimal in both cases (<2 µg/L). However, there were slight differences in terms of N-DBP speciation, where chloropicrin and TCAAm were detected in GAWSS samples, but not in chlorinated samples.

As expected, the *N*-nitrosamine NDMA occurred more frequently and at higher concentrations in the chloraminated GAWSS than in chlorinated waters. NDMA was always detected (100 %) in GAWSS samples, at a higher median and maximum concentration (Table 3) than in the chlorinated systems (Table 2), but still well below the ADWG of 100 ng/L. While the median NDMA concentrations in GAWSS (6.6 and 7.7 ng/L in the main pipeline and the extensions, respectively) were not significantly high (i.e. below 10 ng/L),

they fall within the top 30 % of concentrations in chloraminated waters from 38 Australian drinking water supplies, as we have recently reported (Liew et al. 2015). There were also more detections of other *N*-nitrosamine species in the GAWSS than in the chlorinated waters, although the concentrations of NDMA were slightly lower in the GAWSS than in the chlorinated surface water sites.

As shown in Fig. 3, the concentration distributions of different N-DBP classes were different in the chloraminated GAWSS compared to the chlorinated waters. The Mann–Whitney *U* test, the non-parametric equivalent of the Student *t* test, was performed to determine differences in N-DBP concentrations between the chlorinated systems and the chloraminated GAWSS, and confirmed that there were statistically significant differences ($p < 0.01$) for the concentrations of HANs, HAAs and *N*-nitrosamines between chlorinated systems and the GAWSS.

Variations in the GAWSS distribution system

Within the GAWSS, the extension pipelines were considered to be less ‘well-controlled’ compared to the main pipeline, as they were more remote and had longer residence times, which often led to poorer water quality, including nitrification. Comparison of the occurrence of N-DBPs between the GAWSS main pipeline and the extension pipelines (Table 3) shows comparable concentrations for five halonitriles, DCNM, TCAAm and NDMA. However, the extension pipelines exhibited slightly higher median and maximum concentrations of other N-DBPs than the main pipeline. Specifically, there were higher concentrations of two HAAs (DBAAm, DCAAm) and four *N*-nitrosamines (NDPA, NDMA,

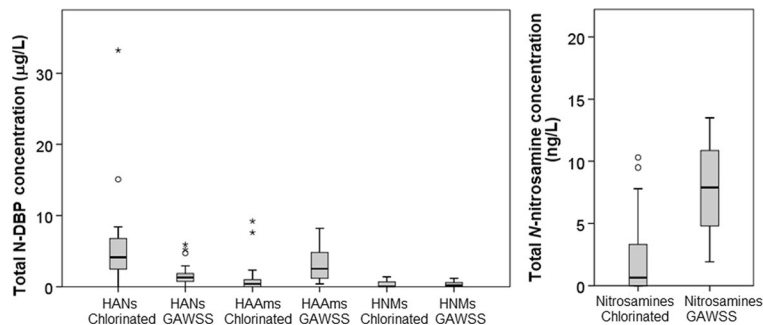


Fig. 3 Box plots showing distributions of N-DBP concentrations in waters from chlorinated sites and the chloraminated GAWSS (all post-disinfection and distribution system samples), expressed as total concentrations (sum of all species within each N-DBP

class). *N*-Nitrosamine concentrations are on a different scale (ng/L) and therefore shown separately to the other N-DBPs. Points (asterisks and open circles) lying outside the box were identified as outliers and were not considered in the distribution

NMOR and NPYR), suggesting that the conditions within the extensions could enhance the formation of some of these N-DBPs. Nitrification has been shown to enhance the concentrations of *N*-nitrosamines and other halogenated DBPs (including NDMA, DCAN and DCAAm) in storage facilities within chloraminated distribution systems, where nitrifying biofilms may contribute DBP precursors (Zeng and Mitch 2016). Along the GAWSS distribution system, there is a section of extension C (Fig. 1) that has historically exhibited evidence of nitrification, as characterised by low chloramine residual, low ammonia concentrations, and elevated concentrations of nitrite and nitrate. In this study, the sample point within the nitrification front exhibited higher concentrations of DBAAm (6.3 $\mu\text{g/L}$), DCAAm (1.9 $\mu\text{g/L}$), NDBA (3.9 ng/L) and NDPA (1.0 ng/L), higher than any other sample measured within the GAWSS distribution system. The concentration of NDMA (8.3 ng/L) was the highest measured in any of the samples taken within the

extension pipelines. However, overall concentrations of HANs were low ($\leq 0.5 \mu\text{g/L}$). While nitrification appears to enhance the concentrations of some N-DBPs, at the same time, formation may also be influenced by other conditions in the distribution system, such as residual chloramine and temperature.

The concentrations of N-DBPs were also assessed along the main GAWSS pipeline, to determine trends in N-DBP formation with increasing distance, as well as with redosing of disinfectant in this long distribution system. Variations in N-DBPs within the extensions were not evaluated to this extent due to the different complex environments and the fewer number of sampling points within each extension. As shown in Fig. 4, the concentrations of HANs and HAAMs changed significantly with distance along the main pipeline (A to F). All the detected HANs followed a similar trend, forming quickly after the initial chloramination point (at location A), subsequently decreasing and then increasing again (after

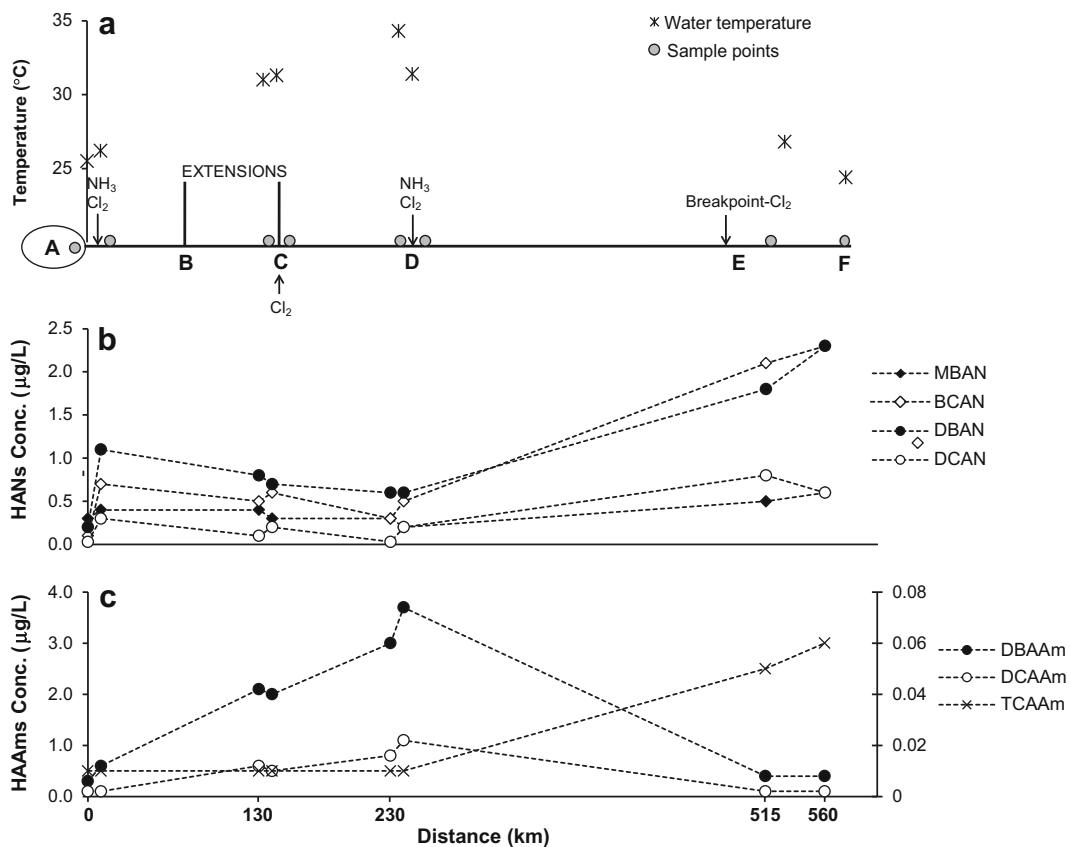


Fig. 4 Variation of the concentrations of **b** HANs and **c** HAAMs with distance along the GAWSS main pipeline (**a**). Distances are approximate only and represent the distance between locations. Temperatures (**a**) at each point represent the temperatures of water

samples. In (c), left vertical axis represents DBAAm and DCAAm concentrations, and right vertical axis represents TCAAm concentration

rechloramination at location D and breakpoint chlorination at E) until the far end of the distribution system. In contrast, the DHAAs (DBAAs and DCAAs) seemed to follow a different trend, increasing steadily and subsequently decreasing towards the end of the distribution system. TCAAs appeared to increase towards the end of the distribution system, but concentrations were very low ($<0.1 \mu\text{g/L}$) compared to DBAAs and DCAAs. Field measurements of disinfectant residual indicated that the water in the main pipeline was mostly chloraminated, until breakpoint chlorination towards the end of the distribution system at location E. The previous evidence supporting the formation of DCAAs over DCAN with chloramination (Huang et al. 2012) and the degradation of both HANs and HAAs with free chlorine (Reckhow et al. 2001) may explain the predominance of HAAs over HANs in the initial portion of the pipeline (locations A to D), and the converse towards the end of the pipeline (E and F), where HAAs formed initially may have degraded into HAs. Another possible factor affecting the occurrence of HAAs and HANs through the distribution system is the temperature. The temperature of waters through the pipeline varied from 24 to 34 °C (Fig. 4), where the highest temperatures were observed around the middle of the pipeline (locations C and D). HANs may have been degraded at the higher temperatures, while the formation of HAAs may have been enhanced. Further analysis of the data with temperatures across all the GAWSS samples ($n = 14$) revealed that there were significant correlations in DBAAs and DCAAs concentrations with temperature ($\rho = 0.725$ and 0.690 , respectively, $p < 0.01$), but correlations with temperature were not significant in the case of HANs. It is possible to conclude that increasing temperatures in the distribution system during chloramination could increase the formation of HAAs. There were no clear trends observed for *N*-nitrosamines or HNMs across the GAWSS distribution system.

Conclusions

This work provides the most comprehensive evaluation of N-DBP concentrations in drinking waters in Australia to date. Various N-DBPs were detected in Western Australian drinking waters from low nanogram per litre (for *N*-nitrosamines) to low microgram per litre (for other N-DBP classes) concentrations, comparable to typical occurrences elsewhere in the

world. However, DBAN was recorded at an elevated concentration ($26.6 \mu\text{g/L}$) in one chlorinated drinking water, which is its highest concentration reported in drinking water to date. Another interesting finding was of the *N*-nitrosamine, NDBA, which was detected more frequently and at higher concentrations than the more commonly studied NDMA, in the chlorinated systems. The use of chlorine versus chloramine disinfection was found to influence the concentrations and speciation of N-DBPs formed. Dihalogenated HANs were the most dominant N-DBP species found in chlorinated waters, but slightly different concentration distributions were observed in the chloraminated GAWSS. *N*-Nitrosamines and HAAs were more prevalent in the GAWSS than in the chlorinated systems.

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

Formation of HANs was correlated to DOC and $\text{NH}_3\text{-N}$ in the pre-disinfection water, but there were no clear relationships between N-DBPs and other components of nitrogen in the pre-disinfection waters. The high concentrations of brominated N-DBPs (i.e. DBAN) produced at one of the groundwater sites (GW4) that contained high DOC, bromide and ammonia in the pre-disinfection water implied that these parameters, alone or combined, could influence the formation of brominated N-DBPs; however, low DOC of the pre-disinfection waters can limit the formation of N-DBPs even in the presence of high bromide. More research is required to assess the relationships between N-DBP formation, bromide and DOC. This study also demonstrates for the first time factors influencing N-DBP occurrence and formation in a large distribution system. Concentrations of N-DBPs can vary significantly with distance in the distribution system, as shown by HAN and HAAs concentrations in the GAWSS, attributable to continuous formation or degradation into other compounds by free chlorine. Varying temperatures

through the distribution system can also influence the formation of N-DBPs, particularly HAAs, where the formation of DBAAm and DCAAm increased with temperature in the distribution system.

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