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Formation and control of nitrogenous DBPs from Western Australian source waters: Investigating the impacts of high nitrogen and bromide concentrations

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ABSTRACT

We studied the formation of four nitrogenous DBPs (N-DBPs) classes (haloacetonitriles, halonitromethanes, haloacetamides, and *N*-nitrosamines), as well as trihalomethanes and total organic halogen (TOX), after chlorination or chloramination of source waters. We also evaluated the relative and additive toxicity of N-DBPs and water treatment options for minimisation of N-DBPs. The formation of halonitromethanes, haloacetamides, and *N*-nitrosamines was higher after chloramination and positively correlated with dissolved organic nitrogen or total nitrogen. N-DBPs were major contributors to the toxicity of both chlorinated and chloraminated waters. The strong correlation between bromide concentration and the overall calculated DBP additive toxicity for both chlorinated and chloraminated source waters demonstrated that formation of brominated haloacetonitriles was the main contributor to toxicity. Ozone–biological activated carbon treatment was not effective in removing N-DBP precursors. The occurrence and formation of N-DBPs should be investigated on a case-by-case basis, especially where advanced water treatment processes are being considered to minimise their formation in drinking waters, and where chloramination is used for final disinfection.

Introduction

Over the past 15 years, the focus of investigations on disinfection by-products (DBPs) in drinking water has gradually shifted from regulated DBPs, such as the trihalomethanes (THMs) and haloacetic acids (HAAs), to other emerging DBPs that are suspected to be more relevant from a human health perspective. Nitrogen-containing DBPs (N-DBPs) are among these emerging DBPs, since their cytotoxicity and genotoxicity in mammalian cells have been found to be much higher than those of THMs and HAAs (Richardson, 2006; Plewa et al., 2004; Moudgal et al., 2000). To-date, most epidemiological studies have not included N-DBPs in their assessment of human health effects (*e.g.* Botton et al., 2015; Salas et al., 2014; Kogevinas et al., 2010; Nieuwenhuijsen et al., 2009; Villanueva et al., 2004). One limited study found no association between exposure to haloacetonitriles (HANs) during pregnancy, and small birthweight (Ileka-Priouzeau et al., 2015). While it is not certain that the *in vitro* effects measured for N-DBPs will translate to human health outcomes, further investigation of N-DBPs has been identified as a research priority by numerous researchers and the US EPA: United

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States Environmental Protection Agency (Krasner et al., 2006; Woo et al., 2002; Richardson et al., 2007; Bull et al., 2006).

N-DBPs are generally found in drinking waters at significantly lower concentrations than THMs and HAAs. Concentrations of haloacetonitriles (HANs), halonitromethanes (HNMs), and haloacetamides (HAMs) are typically reported up to 10–15 μg/L (Krasner et al., 2006; Goslan et al., 2009; Bond et al., 2015; Liew et al., 2016), with HANs often the most frequently detected class (Krasner et al., 2006; Liew et al., 2016). *N*-nitrosodimethylamine (NDMA), the most frequently detected *N*-nitrosamine, is typically detected at concentrations less than 10 ng/L in drinking waters. The concentrations measured are generally lower than published guideline and regulation values (Boyd et al., 2012; Liew et al., 2012a).

The use of chloramine as a disinfectant has been associated with elevated concentrations of N-DBPs relative to chlorination (*e.g.* Kristiana et al., 2014; Bond et al., 2011; Lee et al., 2007), with chloramine itself reported to be an inorganic precursor to N-DBPs (Yang et al., 2010). Nitrogen-enriched fractions of organic matter have also been found to have a higher propensity to form N-DBPs (Bond et al., 2012; Dotson et al., 2009). Algal organic matter is a known major source of dissolved organic nitrogen (DON) in the natural environment, and waters containing higher concentrations of algal organic matter have been reported to form higher concentrations of N-DBPs (Bond et al., 2012; Shah and Mitch, 2012). Roccaro et al. (2011) have further specified that the formation of N-DBPs is associated with the chlorination of nitrogen-containing activated aromatic groups in NOM: Natural organic matter, such as amino acids and N-containing heterocyclic aromatic rings.

Thus far, there is no indication that a single treatment method exists for the management of all N-DBPs, with different treatments reported to be effective for removal of precursors of the different N-DBP classes (Liew et al., 2012a). In contrast to THM precursors, N-DBP precursors tend to be of low molecular weight and low electrostatic charge (Bond et al., 2012), and include free amino acids, as well as the colloidal and hydrophilic fractions of NOM (Mitch et al., 2009). While conventional water treatment has been reported to be moderately effective in removing N-DBP precursors (Bond et al., 2011), treatments that remove lower molecular weight NOM more efficiently, such as activated carbon and riverbank filtration, can sometimes remove higher percentages of HAN and HNM precursors (Liew et al., 2012a).

In this study we investigated the formation four N-DBP classes (HANs, HNMs, HAMs, and *N*-nitrosamines) after chlorination or chloramination of source waters that are rich in N-DBP precursors. DBP formation potential was studied with respect to water quality and organic matter characteristics, providing some insights into the reactivity of the complex mixture of organic matter contained in natural waters and the resulting N-DBP formation. In order to quantify the contribution of N-DBPs to the overall formation of DBPs, the formation of THMs and total organic halogen (TOX) were also measured. Since most source waters in Western Australia contain high concentrations of bromide, we also evaluated the relative and additive toxicity of N-DBPs, in particular brominated N-DBPs. Finally, the effect of conventional water treatment (coagulation–flocculation–clarification–filtration) and ozone–biological activated carbon (O_3 + BAC) treatment on N-DBP formation was investigated using a groundwater source known to contain high concentrations of dissolved organic carbon (DOC), bromide, and ammonia, and which had previously shown high concentrations of HANs in the treated (disinfected) water (Liew et al., 2016).

1. Materials and methods

1.1. Chemicals

All chemicals and standards used in this study were of analytical grade purity, while organic solvents were of HPLC: High Performance Liquid Chromatography grade purity. Specific details on these chemicals are provided in Appendix A (Table S1).

1.2. Study design and sample collection

Four surface waters (HD — reservoir, RV — reservoir, GR — lake, and HE — reservoir) and one groundwater (JD) from Western Australia (WA) were selected for this study. The surface waters were from different climatic regions (HD: North West of WA, RV: South East of WA, GR: South East of WA, HE: East of Perth Metropolitan Area), and all have anecdotally experienced periodic blue-green algal blooms, in particular HD surface water (Antenucci et al., 2016), and thus represent source waters that are likely to be rich in N-DBP precursors. HD, RV, and GR surface waters were each sampled once during the winter season, while HE surface water was sampled in the spring. Sample collection times were determined by availability of operators and accessibility to each site at the commencement of the study. Grab samples were collected from the inlet to the respective treatment plants at these locations. All samples were collected in 4-L amber glass bottles, kept cool (in an ice box) and transported back to the laboratory, where they were refrigerated at 4°C until analysis of water quality parameters, which was typically within 24 hr. Samples were used for formation potential experiments within 1 week of collection.

The groundwater JD (south of Perth metropolitan area) was an ideal source water for meeting two objectives of our study. As well as containing high concentrations of DOC and total N (mostly due to high ammonia concentrations), it has a very high concentration of bromide, allowing for evaluation of the potential toxicity of brominated N-DBPs. This groundwater was treated at a treatment plant where a pilot plant was in operation, which provided an opportunity to evaluate treatment options for minimising the formation of N-DBPs, thus meeting another study objective. At the treatment plant, groundwater JD undergoes pre-chlorination, coagulation, flocculation, clarification and dual media gravity filtration before final disinfection and distribution to customers. Initially, the pilot plant was assembled to evaluate whether the addition of O_3 + BAC treatment improved treated water quality, particularly through improved removal of organic matter, reduced chlorine demand, increased chlorine residual stability, and reduced formation of THMs. For this study, the pilot plant provided an opportunity to evaluate the impact of

O_3 + BAC treatment on the removal of N-DBP precursors. At the pilot plant, three treatment trains were operational with three different types of biologically activated carbon (JD-O1: granular activated carbon (GAC) from an established filter at the treatment plant; JD-O2: coal-based GAC Acticarb GA1000N 8 × 16 mesh; JD-O3: coconut-based GAC Acticarb GC1200N 6 × 12 mesh), but the same ozone dose (average dose 12.7 g O_3/hr; automatic dosing to achieve 0.25 mg O_3/L residual at the end of the ozone contact columns). Further details of the pilot plant are given in Appendix A SI2. At the treatment plant, samples were collected from the inlet to the treatment plant (raw source water, JD-raw), from the inlet to the pilot plant (JD-PF — after pre-chlorination, coagulation–flocculation, and filtration), and after each of the three treatment trains (JD-O1, JD-O2, JD-O3). Protocols for sample collection, transport, and storage were the same as those for the surface water samples, except for the addition of sodium sulphite to quench any chlorine residuals present in these samples.

1.3. Disinfection by-product formation potential (DBP FP) experiments

The raw surface waters and the raw and treated waters from the groundwater treatment plant were tested for formation of N-DBPs, THMs and TOX after chlorination or chloramination. A working chlorine solution was prepared by dilution of commercially available sodium hypochlorite solution. A concentrated, preformed monochloramine solution was prepared by adding together equal volumes of buffered (pH 8, 30 mmol/L borate buffer) hypochlorite solution and ammonium sulphate solution in a 4:1 Cl_2:N mass ratio, in an ice-bath, with stirring. A working monochloramine solution was prepared by dilution of the concentrated solution.

Batch chlorination and chloramination experiments were carried out at pH 7 and 8, respectively, at room temperature, using phosphate buffer (10 mmol/L) and sodium hydroxide solution for pH adjustment. Disinfection was undertaken on a reactivity basis, following the method developed by Krasner et al. (2004), where chlorine and chloramine doses were calculated using the following equations:

$$\text{Chlorine dose } (\text{mg/L } Cl_2) = 3 \times [\text{TOC}] + 7.6 \times [NH_3\text{–N}] + 10 \text{ mg/L, pH 7}$$

$$\text{Monochloramine dose } (\text{mg/L } Cl_2) = 3 \times [\text{TOC}] \text{ mg/L, pH 8}$$

The chlorine and chloramine doses used for each raw water sample are given in Appendix A SI3. After a reaction time of 72 hr, sub-samples were collected and the disinfectant residual in these samples was quenched with appropriate quenching agents for each class of DBPs (Appendix A SI4) prior to DBP analysis.

1.4. Analysis of DBPs

The chlorinated and chloraminated samples were analysed in duplicate for 4 THMs, 6 HANs, 7 HNMs, 5 HAMs, 8 *N*-nitrosamines, and halogen-specific TOX (Appendix A SI4). The 5 DBP classes were analysed by 4 separate analytical methods using gas chromatography–mass spectrometry (GC–MS) following different organic extraction methods for different DBP classes. THMs were extracted with solid-phase microextraction (SPME) based on a simplified version of the method described in Allard et al. (2012). HANs were analysed using a method described by Kristiana et al. (2012), also employing SPME. HNMs and HAMs were analysed together in a method described by Liew et al. (2012b), where liquid–liquid extraction was employed. *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 ionization. Halogen-specific TOX (TOCl: Total organic chlorine; TOBr: Total organic bromine; TOI: Total organic iodine) was analysed following the method described in Neale et al. (2012), where samples were acidified to pH 2 and adsorbed onto activated carbon which was then combusted, and the hydrogen halide gases produced were trapped in ultrapure water and analysed by on-line ion chromatography. Details of the limits of detection (LODs) of the analytical methods used to measure DBPs in this study are given in Appendix A SI4.

1.5. Analysis of water quality parameters

The water samples were analysed for UV_{254} absorbance, and DOC, bromide, iodide, ammonia, nitrate, nitrite, and total nitrogen concentrations using standard methods (Clesceri et al., 1998). UV_{254} absorbance was determined using an Agilent Cary 60 UV/Vis Spectrophotometer with a 1-cm quartz cell (Standard Method 5910B). DOC was determined by the UV/persulphate oxidation method, using a Shimadzu TOC Analyser TOC-VWS (Standard Method 5310C). Bromide was determined by ion chromatography (Standard Method 4110B). Total nitrogen content, ammonia, nitrate and nitrate were determined by flow injection analysis (FIA) using Standard Methods 4500N-C, 4500NH3-H, and 4500NO3-I, respectively, by a commercial laboratory. Dissolved organic nitrogen (DON) was determined as the difference between total dissolved nitrogen and inorganic nitrogen (sum of nitrate, nitrite and ammonia). $SUVA_{254}$ was calculated by dividing UV_{254} absorbance by the DOC concentration, according to the equation: $SUVA_{254} = 100 \times UV_{254} / DOC$ (L/mg/m). Amino acids were analysed by liquid chromatography with mass spectrometric detection (LC–MS) after pre-concentration with solid-phase extraction (How et al., 2014).

The organic matter in the samples was also characterised using a liquid chromatograph (LC) equipped with organic carbon, UV_{254} absorbance, and organic nitrogen detectors (Model 8 LC–OCD–OND, DOC Labor, Germany), following Huber et al. (2011). Using this method, organic matter is passed through a column, where some organic carbon is retained in the column (hydrophobic organic carbon — HOC) and the rest elutes through the column (hydrophilic — HIC; no hydrophobic interaction with the column) (Huber et al., 2011). Within the hydrophilic fraction, the organic matter was fractionated into five major size fractions (biopolymers [BIO], humic-like substances [HS], building blocks [BB], low molecular weight neutrals [LMWN], and low molecular weight organic acids [LMWA]) using a Toyopearl TSK HW-50S column. The LC–OCD–OND system provided information on the fractions of DOC and their DON content, as well as the UV absorbance of the size fractions, enabling detailed physico-chemical characterisation of the fractions. For example, the aromaticity of the HS fraction

and an estimate of the protein content in the BIO fraction were obtained.

2. Results and discussion

2.1. Characterisation of source water samples

The source (raw) waters selected for this study came from different climatic regions, hence significant differences in water quality and organic matter characteristics were expected (Table 1). When comparing general water quality, the groundwater sample, JD, had comparable DOC and total N concentrations to the surface water sources, but contained higher concentrations of bromide (935 μg/L) than the surface water samples (37–370 μg/L). For surface waters, there was a trend of decreasing $SUVA_{254}$ with increasing DOC concentration. Coincidentally, there was a correlation between $SUVA_{254}$ values of the source waters and their bromide concentrations (R^2 = 0.76; Pearson's correlation), which meant that any parameters that correlated with $SUVA_{254}$ also had some correlation with bromide concentration. No other water quality parameter was found to correlate with bromide concentration.

Total N concentrations in the source waters ranged from 0.32 to 1 mg/L, with significant variation in the composition of total N. Only groundwater JD had a high concentration of ammonia, while all surface waters had ammonia at or below the detection limit. The two surface waters with the highest

Table 1 – Water quality and organic matter characteristics of source waters.

	Surface water				Groundwater
	HD	RV	GR	HE	JD
	North West WA	South East WA	South East WA	Perth Metro East	Perth Metro South
Organic carbon					
DOC (mg/L)	4.10	5.80	2.16	2.64	3.88
UV_{254} (1/cm)	0.084	0.088	0.066	0.106	0.212
$SUVA_{254}$ (L/mg/m)	2.0	1.5	3.1	4.0	5.5
Hydrophobic fraction [a]					
DOC (mg/L)	2.58	2.76	1.55	0.59	0.83
% DOC	43	33	48	17	14
Hydrophilic fraction [b]					
DOC (mg/L)	3.47	5.64	1.66	2.84	5.0
% DOC	57	67	52	83	86
Biopolymers					
DOC (mg/L)	0.27	2.14	0.07	0.21	0.03
% DOC	4.5	25	2	6	0.4
Humic-like					
DOC (mg/L)	2.27	2.36	1.0	1.65	3.59
% DOC	37	28	31	48	62
Building blocks					
DOC (mg/L)	0.54	0.69	0.32	0.51	0.69
% DOC	9	8	10	15	12
Low MW neutrals					
DOC (mg/L)	0.39	0.46	0.28	0.47	0.69
% DOC	6.5	5.5	9	14	12
Nitrogen					
Total N (mg/L)	0.40	0.32	1.0	0.52	0.40
Ammonia (mg/L)	0.01	<0.01	<0.01	<0.01	0.35
Nitrate (mg/L)	<0.01	<0.01	0.8	0.2	0.01
Nitrite (mg/L)	<0.01	<0.01	0.01	<0.01	<0.01
DON (mg/L) [c]	0.39	0.32	0.19	0.32	0.04
DON in biopolymers fraction [d] (μg/L N)	28	76	3	39	24
DON in humic-like fraction [d] (μg/L N)	161	101	23	56	122
Total DON [e] (μg/L N)	189	177	26	95	146
Total free amino acids (μg/L N)	15	16	26	57	73
Halide ions					
Bromide (μg/L)	225	98	37	370	935

DOC: dissolved organic carbon; DON: dissolved organic nitrogen; LC: liquid chromatography; OCD: organic carbon detection; OND: organic nitrogen detection; UV: Ultraviolet; SUVA: Specific Ultraviolet Absorbance.

[a] DOC = hydrophobic + hydrophilic fractions.

[b] Hydrophilic fraction = biopolymers + humic-like + building blocks + low MW neutral fractions.

[c] Obtained by calculation DON = Total N – sum of inorganic N.

[d] Measured by LC–OCD–OND.

[e] Sum of DON in biopolymers and humic-like fractions, measured by LC–OCD–OND.

total N concentration (GR and HE) were the only samples to have measurable nitrate, which contributed to 80% and 38% of total N, respectively. All surface waters had higher concentrations of DON than the groundwater JD. There was no correlation between the concentrations of total N and DON, but there was moderate correlation between DON and DOC (R^2 = 0.68; Pearson's correlation).

LC–OCD–OND analysis provided information on the composition of organic carbon and nitrogen in fractions of the samples. The results showed that the percentage of hydrophilic carbon (HIC; organic carbon that is not retained in the column and elutes through the column), which consisted of BIO, HS, BB and LMWN fractions, was greater than 50% for all samples, with the surface water HE and groundwater JD both having greater than 80% of HIC (Table 1). The RV sample had the highest proportion of the BIO fraction (25%); this, as well as the low $SUVA_{254}$ associated with the sample, suggests that the DOC was more likely to have been impacted by microbiological activity than the DOC in the other samples. In contrast, the JD groundwater had the lowest BIO concentration (0.4%) but the highest HS fraction at 62%. All source waters contained similar proportions of BB carbon (8%–15%) (Table 1). While the HD water had only a low BIO concentration and a moderate HS fraction, the N content of the latter fraction was significantly higher than for other samples. Thus, the combined N content from the BIO and HS fractions (*i.e.* total DON concentration) was highest for the HD water, which could indicate that the HD water would have a higher potential to form N-DBPs than the other source waters. Conversely, GR water, which had the lowest total DON concentration, would be expected to have relatively low potential to form N-DBPs.

In order to further characterise the DON fraction of the water samples, free amino acids were also analysed. Amino acids were expected to be important components of DON, however several amino acids had limits of detection >50 μg N/L (*e.g.* lysine, alanine, asparagine, threonine, see Appendix A SI5), which was significant given that total values of detected amino acids were 15–73 μg N/L (Table 1). Therefore, total free amino acid concentrations reported here are likely to underestimate true values, and this may explain why the total free amino acids measured in the samples accounted for only 4%–18% of DON (as measured by LC–OCD–OND, sum of DON in BIO and HS fractions) in the surface waters, and 59% of DON in JD groundwater. The concentrations of total free amino acids in GR, HE, and JD waters were higher than the DON concentrations measured in their respective BIO fractions (Table 1), suggesting that the majority of free amino acids belonged to the HS fraction. Overall, there was no significant correlation between amino acid content and DON, which is consistent with the data reported by Mitch et al. (2009).

2.2. Formation of DBPs after chlorination and chloramination of source waters

N-DBP, THM and TOX formation potential experiments were carried out for all source waters over 3 days after both chlorination and chloramination (Figs. 1 and 2; Appendix A SI6). Following the method developed by Krasner et al. (2004), the disinfection doses used were typically higher than those used in real drinking water systems (Table S2, Appendix A).

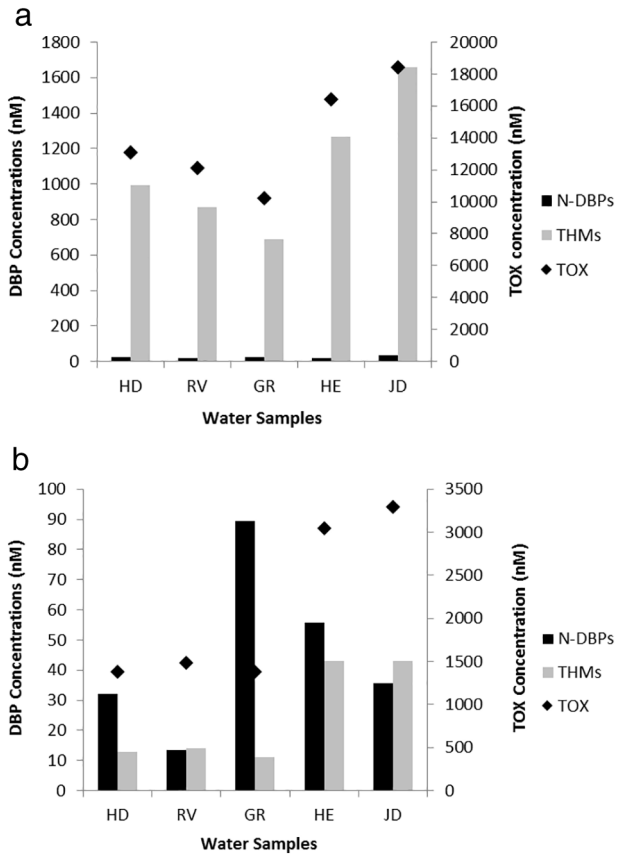

Fig. 1 – The concentrations of total nitrogenous disinfection by-product (N-DBP), total trihalomethanes (THMs), and total organic halogen (TOX) after (a) chlorination and (b) chloramination of source waters over 3 days.

Overall, the total amount of measured halogenated DBPs contributed to only a small proportion of TOX after both chlorination and chloramination, demonstrating that there was a large proportion of 'unknown' TOX (90%–93% of 'unknown' TOX after chlorination, 93%–98% after chloramination). Kristiana et al. (2015) also found high proportions of unknown TOX (up to 80% after chlorination and 90% after chloramination) in similar Western Australian systems. Hua et al. (2015) reported lower proportions of unknown TOX (20%–50% after chlorination and 65%–80% after chloramination). In their study, they also measured HAAs, a known major class of DBPs (30%–40% of TOX in chlorination; 15%–30% of TOX in chloramination), which may explain why the percentage of unknown TOX they reported was lower than in the current study. In our current study, total THMs contributed a higher percentage of TOX in chlorinated waters (7%–10%) than in chloraminated waters (0.8%–1.4%, Supporting Information SI7), while total halogenated N-DBPs contributed a higher percentage of TOX in chloraminated waters (1%–7%) than in chlorinated waters (0.1%–0.2%). The lower contribution of THMs to TOX in chloramination was expected, since chloramine forms significantly lower concentrations of THMs than chlorine. For individual classes of N-DBPs, HAN concentrations were higher after chlorination, while HNM, HAM, and *N*-nitrosamine concentrations were higher after chloramination (Fig. 2; Appendix A SI6). These trends are consistent with previously reported general trends of DBP formation from chlorination and

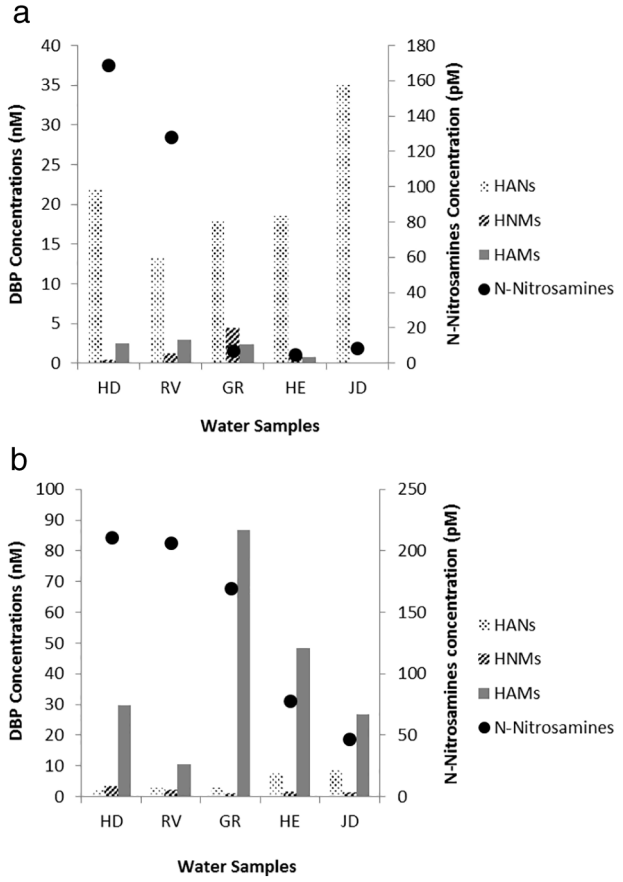

Fig. 2 – The concentrations of N-DBPs after (a) chlorination and (b) chloramination of source waters over 3 days.

chloramination (Bond et al., 2011), and occurrence data from Western Australian distribution systems (Liew et al., 2016).

While there was a strong correlation (evaluated by Pearson's correlation) between the formation of total THMs and TOX in both chlorination (R^2 = 0.99) and chloramination (R^2 = 1.0) experiments (Appendix A SI8), these correlations were largely controlled by the concentrations of brominated THMs and TOBr. A similar relationship was not observed for the formation of total halogenated N-DBPs (sum of molar concentrations of HANs, HNMs, and HAMs), although there were moderate to strong correlations between the concentrations of total HANs and TOX in both chlorination (R^2 = 0.75) and chloramination (R^2 = 1.00) experiments. The concentrations of the other classes of N-DBPs did not correlate with TOX. This may suggest that TOX, THMs, and HANs have similar types of organic precursors, whereas other parameters, *e.g.* concentration of monochloramine, may have greater influence on the formation of other N-DBPs.

The parameter $SUVA_{254}$ has been used as a surrogate for the aromatic content of aquatic organic matter, which has been associated with its reactivity towards oxidants or disinfectants (Croué et al., 2000); while higher concentrations of bromide (or higher ratios of bromide to DOC) have been associated with higher concentrations of brominated DBPs (Watson et al., 2015a; Kristiana et al., 2009). JD water consistently formed the highest concentrations of THMs in both chlorination and chloramination experiments, and it also had the highest $SUVA_{254}$ value and bromide concentration. This suggests that $SUVA_{254}$ and bromide concentration may be important indicators for THM formation. Strong correlations between the concentrations of TOX and $SUVA_{254}$ (R^2 = 0.80 in chlorination, R^2 = 0.89 in chloramination; Appendix A SI8), and between total THMs and $SUVA_{254}$ (R^2 = 0.82 in chlorination, R^2 = 0.85 in chloramination) were observed (Appendix A SI8), confirming this potential relationship. Hua et al. (2015) also reported moderate to strong correlations between the concentration of TOX and $SUVA_{254}$ after chlorination (R^2 = 0.79) and chloramination (R^2 = 0.67) of NOM fractions isolated from surface waters.

Strong correlations were also observed between the concentrations of total HAN and $SUVA_{254}$ in both chlorinated (R^2 = 0.82) and chloraminated (R^2 = 0.91) waters. The formation of HANs from aromatic moieties in NOM in chloramination experiments has been demonstrated by Le Roux et al. (2016), supporting the possibility of correlation between HAN concentrations and $SUVA_{254}$. However, the increased formation of brominated HANs in chlorinated waters also probably reflects the stronger influence of bromide concentration in DBP formation during chlorination compared to chloramination.

The formation of the other classes of N-DBPs (*N*-nitrosamines, HNMs and HAMs) did not correlate strongly with $SUVA_{254}$. In fact, there was an inverse correlation between total *N*-nitrosamine concentration and $SUVA_{254}$ in both chlorinated (R^2 = −0.79) and chloraminated (R^2 = −0.96) waters. This result is consistent with previous studies showing that NDMA formation does not correlate with $SUVA_{254}$ nor the aromatic content of NOM (Dotson et al., 2009; Lee et al., 2007). Correlations between total HNM or HAM and $SUVA_{254}$ were also low or negative, which suggests that the precursors of these N-DBPs also did not come from aromatic organic compounds within NOM.

For N-DBPs, higher organic nitrogen content of source waters has been found to lead to increased N-DBP formation (Dotson et al., 2009). HD water, which had the highest concentration of DON among the source waters, consistently produced the highest concentrations of *N*-nitrosamines in both chlorination and chloramination experiments, but not for other N-DBP classes. Overall, RV water had the lowest total N-DBP concentration, although RV water had relatively high DON and higher concentrations of NOM fractions that have been associated with N-DBP precursors (*i.e.* BIO fraction) than the other source waters. Overall, there were no consistent correlations between the concentrations of halogenated N-DBPs measured and the nitrogen content in the water samples (Appendix A SI8). Correlations of N-DBP formation with DON were typically higher in chlorination experiments compared to chloramination experiments, possibly reflecting that monochloramine provides an additional source of nitrogen during chloramination.

The species distribution of DBPs measured in the source waters varied with the disinfectants used (Figs. 1 and 2, Appendix A SI6), with bromide concentration playing an important role for all halogenated DBPs and N-DBPs, as well as TOX. In chlorinated samples, the molar ratio of Br to Cl incorporated into the measured DBPs was 10%–40%, while the corresponding range for chloraminated samples was 1%–15%. These trends are consistent with the relatively low concentrations of bromide (37–370 μg/L) in the source waters and the high

concentrations of chlorine (18–28 mg/L) and chloramine (8–18 mg/L) added. The groundwater sample, JD, has a much higher concentration of bromide (935 μg/L), and the molar ratio of Br to Cl incorporated into the measured DBPs was 70%, while the corresponding range for chloraminated samples was 35%. A similar pattern was also seen for the increased contribution of TOBr in TOX in JD water compared to surface waters (Tables S6 and S7; Appendix A SI6). In general, strong correlations were observed between the concentrations of bromide and brominated DBPs (Tables S10 and S11; Appendix A SI8) in both chlorinated and chloraminated waters. JD water was the only water to form dibrominated N-DBPs (dibromoacetonitrile (DBAN) after chlorination, and dibromoacetamide (DBAM) and dihalonitromethane (DHNM) after chloramination). The formation of elevated concentrations of brominated DBPs is a potential public health concern, since many brominated DBPs have been shown to be more cytotoxic and genotoxic than their chlorinated analogues (Sawade et al., 2016; Watson et al., 2015b; Plewa et al., 2008; Richardson et al., 2007).

2.3. Toxicity assessment of chlorinated and chloraminated source waters

The toxicity of some DBPs has been studied and reported, and comparative toxicity values of some DBPs have been reported (Zeng et al., 2016 and references therein). These data allow for toxicity assessment of disinfected waters. The presence of bromide in source waters promotes the formation of brominated DBPs, which have been reported to be more cytotoxic and genotoxic (Sawade et al., 2016; Plewa et al., 2004, 2008) than their chlorinated analogues. Following the approach reported by Zeng et al. (2016), a toxicity assessment was conducted on the DBPs produced from chlorination and chloramination of the source waters (Table 2). The potential contributions of the DBPs to the toxicity of the water were estimated by dividing their measured concentrations by concentrations determined in toxicological assays to be associated with adverse health outcomes (Chinese hamster ovary (CHO) cell LC_{50} values for THMs, HANs, HNMs, and HAMs; (LECR: Lifetime excess cancer risk) $LECR_{50}$ values for *N*-nitrosamines) (Zeng et al., 2016). Therefore, this measure of toxicity only considered *in vitro* cell toxicity, which may be different to *in vivo* toxicity determined by animal studies. The calculated DBP additive toxicities are presented in Table 2. There was a strong correlation between bromide concentration and the overall DBP additive toxicity in both chlorinated ($R^2 = 0.92$) and chloraminated ($R^2 = 0.94$) waters, demonstrating the impact of bromide on the toxicological properties of disinfected waters.

The overall DBP additive toxicity was found to be higher in chlorinated waters than chloraminated waters (3–12 times higher), however, the toxicity of *N*-nitrosamines was higher in chloraminated waters (up to 22 times higher). The major contributor to overall calculated additive toxicity of chlorinated waters was the HANs (70%–96%), with THMs contributing between 3% and 22%, despite the fact that the molar concentrations of THMs were between 38 and 67 times higher than the molar concentrations of the HANs. Zeng et al. (2016) also found that HANs exhibited the highest additive toxicity in recycled waters. In chloraminated waters, the contribution of THMs to overall additive toxicity was always less than 2%, with HANs contributing between 36% and 70%, and *N*-nitrosamines contributing between 2% and 45%. The contribution of HAMs to the calculated toxicity was also significant, ranging between 5% and 34%. The relatively minor contribution of *N*-nitrosamines to toxicity in this study is illustrated by considering the source waters JD and HE, which had the highest overall additive toxicity of all chloraminated samples, but the lowest measured total *N*-nitrosamine concentrations. The increased toxicity from these disinfected source waters resulted from detection of bromochloroacetonitrile (BCAN) in addition to dichloroacetonitrile (DCAN), again highlighting the influence of brominated DBPs on overall toxicity.

Table 2 – DBP additive toxicities [a] in chlorinated and chloraminated source waters.

DBP class	Additive toxicity				
	HD	RV	GR	HE	JD
Chlorination					
THMs	1.09×10^{-4}	9.24×10^{-5}	7.32×10^{-5}	1.51×10^{-4}	2.23×10^{-4}
HANs	4.67×10^{-4}	2.94×10^{-4}	3.84×10^{-4}	8.64×10^{-4}	6.24×10^{-3}
HNMs	n.d.	1.57×10^{-6}	6.55×10^{-6}	6.59×10^{-7}	n.d.
HAMs	1.25×10^{-6}	1.50×10^{-6}	1.21×10^{-6}	3.63×10^{-7}	1.13×10^{-7}
Nitrosamines	3.69×10^{-5}	2.95×10^{-5}	1.06×10^{-6}	2.87×10^{-7}	5.19×10^{-7}
All DBPs	6.15×10^{-4}	4.20×10^{-4}	4.66×10^{-4}	1.02×10^{-3}	6.47×10^{-3}
Chloramination					
THMs	1.25×10^{-6}	1.43×10^{-6}	1.17×10^{-6}	4.41×10^{-6}	4.93×10^{-6}
HANs	3.97×10^{-5}	4.76×10^{-5}	4.76×10^{-5}	2.37×10^{-4}	3.72×10^{-4}
HNMs	3.51×10^{-6}	3.89×10^{-6}	5.01×10^{-7}	2.61×10^{-6}	1.60×10^{-6}
HAMs	1.55×10^{-5}	5.54×10^{-6}	4.51×10^{-5}	2.51×10^{-5}	1.38×10^{-4}
Nitrosamines	4.96×10^{-5}	4.81×10^{-5}	3.91×10^{-5}	1.80×10^{-5}	1.17×10^{-5}
All DBPs	1.10×10^{-4}	1.07×10^{-4}	1.33×10^{-4}	2.88×10^{-4}	5.28×10^{-4}

n.d.: not detected; DBP: disinfection by-product; THMs: trihalomethanes; HANs: haloacetonitriles; HNMs: halonitromethanes; HAMs: haloacetamides.

[a] DBP additive toxicity was calculated according to the method published by Zeng et al. (2016).

2.4. Effect of drinking water treatment on organic matter characteristics and N-DBP formation

Analysis of DOC through the JD groundwater treatment plant (GWTP) showed that the conventional treatment process (coagulation–flocculation–clarification–filtration) removed the majority of DOC in the source water (70% removal), while additional removal from O_3 + BAC was small (2%–15%) (Table 3 and Appendix A SI9). While UV_{254} decreased with treatment, $SUVA_{254}$ notably increased following conventional treatment, suggesting that aromatic compounds were not removed as well as aliphatic NOM. $SUVA_{254}$ further increases after O_3 + BAC at JD-O1, which employed GAC from an established filter at the treatment plant, but decreased at JD-O2 and JD-O3, where new coal-based activated carbon and coconut-based activated carbon were employed, respectively. Results from LC–OCD–OND analysis showed that JD waters had similar compositions (*i.e.* size fractions) of organic carbon (Table 3) before and after treatment, which suggests that the treatment processes employed at the plant did not preferentially remove different size fractions of organic carbon. There was also a strong correlation between $SUVA_{254}$ and DOC concentration ($R^2 = 0.95$) in these samples, suggesting that the portion of DOC removed by the treatment processes was mostly the UV_{254}-active fraction of NOM. This suggests that, while the size composition of organic carbon remained relatively unchanged, the activated carbon filters at JD-O2 and JD-O3 were able to reduce $SUVA_{254}$ by removing more DOC than at JD-O1. These newer filters may have higher capacity and efficiency in removing NOM. There was no significant change in the concentration of overall DON following treatment (Table 3). Since significant amounts of DOC were removed, the overall DON/DOC ratios in the waters increased following treatment. However, the amount of DON measured by LC–OCD–OND did decrease with treatment, particularly for the HS

Table 3 – Water quality and organic matter characteristics of JD groundwater samples.

	JD-raw	JD-PF	JD-O1	JD-O2	JD-O3
Organic carbon					
DOC (mg/L)	3.88	1.17	1.14	1.07	0.99
UV_{254} (1/cm)	0.212	0.073	0.077	0.055	0.031
$SUVA_{254}$ (L/mg/m)	5.5	6.2	6.8	5.1	3.1
Hydrophobic fraction [a]					
DOC (mg/L)	0.83	0.48	0.43	0.48	0.38
% DOC	14	18	17	18	15
Hydrophilic fraction [b]					
DOC (mg/L)	5.0	2.22	2.13	2.16	2.13
% DOC	86	82	83	82	85
Biopolymers					
DOC (mg/L)	0.03	0.002	0.01	0.01	0.02
% DOC	0.4	0.1	0.6	0.3	0.8
Humic-like					
DOC (mg/L)	3.60	1.41	1.32	1.35	1.36
% DOC	62	52	52	51	54
Building blocks					
DOC (mg/L)	0.69	0.32	0.38	0.41	0.34
% DOC	9	8	10	15	12
Low MW neutrals					
DOC (mg/L)	n.q.	n.q.	n.q.	n.q.	n.q.
% DOC	–	–	–	–	–
Nitrogen					
Total N (mg/L)	0.40	0.32	0.26	0.24	0.25
Ammonia (mg/L)	0.35	0.26	0.16	0.16	0.16
Nitrate (mg/L)	0.01	0.01	0.04	0.03	0.04
Nitrite (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01
DON (mg/L) [c]	0.04	0.05	0.06	0.05	0.05
DON in biopolymers fraction [d] (μg/L N)	24	19	17	n.q.	n.q.
DON in humic-like fraction [d] (μg/L N)	122	52	27	32	13
Total DON [e] (μg/L N)	146	71	44	32	13
Total free amino acids (μg/L N)	73	16	34	30	18
Halide ions					
Bromide (μg/L)	935	1200	1288	1290	1284

n.q.: not quantifiable, signal too close to the noise level; DOC: dissolved organic carbon; DON: dissolved organic nitrogen; LC: liquid chromatography; OCD: organic carbon detection; OND: organic nitrogen detection; UV: Ultraviolet; SUVA: Specific Ultraviolet Absorbance.

[a] DOC = hydrophobic + hydrophilic fractions.

[b] Hydrophilic fraction = biopolymers + humic-like + building blocks + low MW neutral fractions.

[c] Obtained by calculation DON = Total N – sum of inorganic N.

[d] Measured by LC–OCD–OND.

[e] Sum of DON in biopolymers and humic-like fractions, measured by LC–OCD–OND.

fraction, which was better removed than the other fractions. The reduction in DON was consistent with the trend of decreased DOC in the HS fraction. There was no clear trend on the effect of treatment on amino acid content (Table 3). The concentrations of total free amino acids decreased following conventional treatment (78% removal), but increased following O_3 + BAC treatment. The increase may be caused by the introduction of proteinaceous materials originating from bacterial growth in BAC column, which could be released from the BAC column itself. The release of free amino acids from lysis of bacterial or algal cells during the sand filtration process has been reported previously (LeCloirec et al., 1986).

The concentrations of bromide increased during conventional treatment, but remained relatively constant through O_3 + BAC treatment. Bromide can exist as an impurity in sodium hypochlorite. However, in this case, the bromide impurity would have been present in percent concentrations to cause the increase observed, which is unlikely. While the cause of the increase observed during conventional treatment is not known, however, historical data from this treatment plant indicates that bromide concentrations can increase by 20%–50% between the raw water sample point and the post-clarification sample point (Nottle, 2013). Bromide concentrations then remain unchanged through the dual media filters. Therefore, while we cannot explain the increase in bromide concentration, the observed increase does not appear to be caused by instrumental error or analytical interferences. Overall, it is clear that there is no net removal of bromide during either conventional or O_3 + BAC treatment. Consequently, the bromide to DOC ratio continued to increase during treatment.

The resulting increase in the bromide to DOC ratio led to higher formation of brominated DBPs and TOBr, relative to TOCl, in the laboratory disinfection experiments that were subsequently carried out (Table 4). This effect was more dramatic for chloramination experiments, where, for example, the ratio of Br to Cl incorporated into DBPs increased from 0.3 (JD-raw) to 20 (JD-PF), and the proportion of TOBr in TOX increased from 14% to 90%. In the corresponding chlorination experiments, the ratio of Br to Cl incorporated into the measured DBPs increased from 0.7 (JD-raw) to 1.5 (JD-PF), while the proportion of TOBr in TOX increased from 32% (JD-raw) to 48% (JD-PF). While the additional treatment by O_3 + BAC did not significantly change bromide concentrations, the bromide to DOC ratio did increase further, causing additional increases in the ratio of Br to Cl incorporated into DBPs and the proportion of TOBr in TOX (Table 4). Many studies have shown that higher percentages of brominated DBPs were produced with increasing bromide to DOC ratio (*e.g.* Roccaro et al., 2014; Hua et al., 2006; Krasner et al., 1996), consistent with the kinetics of the oxidation of bromide and the reactivity of oxidised bromide towards NOM (Criquet et al., 2015; Heeb et al., 2014).

Laboratory chlorination and chloramination of waters from JD GWTP showed a variety of trends in DBP formation, which were functions of the treatment process and

Table 4 – Water quality characteristics relative to DOC and the specific yields of DBPs formed in chlorinated and chloraminated JD groundwater samples.

Parameter	JD-raw	JD-PF	JD-O1 (Established GAC)	JD-O2 (Coal-based GAC)	JD-O3 (Coconut GAC)
Water quality parameters					
Br/DOC	241	1028	1131	1204	1292
TN/DOC	0.10	0.27	0.23	0.22	0.25
Org N/DOC	0.01	0.04	0.05	0.05	0.05
DBPs from chlorination					
TTHM/DOC	426	478	455	365	485
THM BIF	1.22	1.80	1.84	1.78	1.87
TOCl/DOC	3201	1848	2474	1307	1616
TOBr/DOC	1534	1735	1910	1721	2173
TOX/DOC	4747	3571	4380	3037	3803
THAN/DOC	9.1	2.3	5.8	2.7	3.8
DHAN BIF	1.1	1.0	1.6	1.5	1.5
TNitroso/DOC	2.3	25.6	4.6	6.7	9.1
DBPs from chloramination					
TTHM/DOC	11.1	45.5	12.4	30.5	18.8
THM BIF	1.07	2.77	2.64	2.70	2.69
TOCl/DOC	699	18	13	14	12
TOBr/DOC	115	347	95	418	249
TOX/DOC	849	385	108	425	257
THAN/DOC	2.25	0.00	0.67	0.13	0.52
DHAN BIF	0.25		1.00	1.00	1.00
THNM/DOC	0.36	1.09	1.08	1.27	1.31
THAM/DOC	6.90	113.05	7.88	6.25	6.19
TNitroso/DOC	12.13	3.10	42.83	7.40	60.52

GAC: granular activated carbon; TTHM: total trihalomethane; DOC: dissolved organic carbon; THM: trihalomethane; BIF: bromine incorporation factor; TOX: total organic halogen; TN: Total Nitrogen; TOCl: Total Organic Chlorine; TOBr: Total Organic Bromine; THAN: Total haloacetonitriles; DHAN: dihaloacetonitrile; TNitroso: Total *N*-nitrosamines.

disinfectant used (Fig. 3, Table 4, Appendix A SI6 and SI9). The conventional treatment reduced the formation of TOX by 77% and 86% in chlorination and chloramination, respectively (Table S12, Appendix A SI9). Total THM formation was reduced by 66% in chlorination, but was slightly increased by 23% in chloramination (Table S12, Appendix A SI9). The latter increase in THM formation could be attributed to large increases in the concentrations of chlorodibromomethane (1.6 times increase) and bromoform (24 times increase) (Appendix A SI6), resulting from the increased bromide concentrations and thus the bromide to DOC ratio. However, there was no correlation between bromide and DBP concentrations for JD groundwaters (data not shown). The formation of brominated THMs could also result from the formation of highly reactive bromamines, which may be possible during chloramination at such high concentrations of bromide (Heeb et al., 2014). Following conventional treatment, the formation of total N-DBPs was reduced by 92% during chlorination, but increased by four fold during chloramination (Table S12, Appendix A SI9), further highlighting the contribution of chloramine towards the formation of N-DBPs. The increase in N-DBP formation after conventional treatment was largely due to the large increase in DBAM (from 1.5 nmol/L in JD-raw to 128 nmol/L in JD-PF), attributed to the increase in Br to DOC ratio (from 241 μg Br/mg DOC in JD-raw to 1028 μg Br/mg DOC in JD-PF), analogous to the increase in brominated THMs. Additional O_3 + BAC treatment had different effects on different classes of DBPs. O_3 + BAC reduced total THMs (TTHM) formation further by 7%–30% and 38%–73% in chlorination and chloramination, respectively. There was no clear trend in the formation of TOX after O_3 + BAC treatments, but O_3 + BAC did increase the formation of total N-DBPs in both chlorination and chloramination experiments by 7%–145% and 93%–95%, respectively. Since DBP formation after chlorination and chloramination can be considered as representative of the presence of DBP precursors in the water, the increase in total N-DBPs suggests that O_3 + BAC was not effective in removing N-DBP precursors, and it may have introduced more N-DBP precursors. The absence of correlation between DOC and DON concentrations in these samples further highlights the different behaviours of these parameters under the same water treatment processes. There was no correlation between water quality parameters and the formation of DBPs in chlorinated and chloraminated JD waters (Table 4). However, the bromine incorporation factor (BIF) in THMs (Table 4) consistently increased with increasing bromide concentration in these samples.

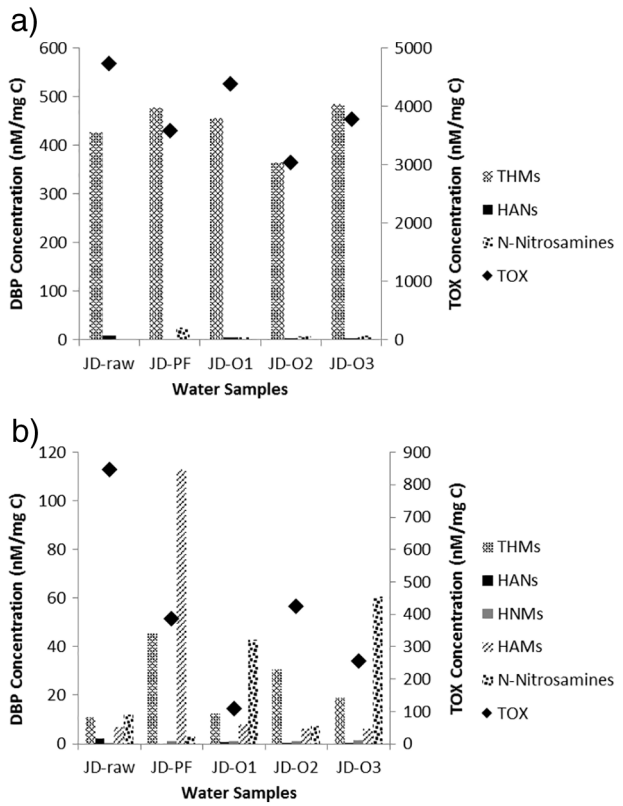

Fig. 3 – The formation of DBPs per mg carbon after 3 day (a) chlorination and (b) chloramination of JD source water (JD-raw), and conventional (JD-PF) and ozone–biological activated carbon (BAC) treatments (JD-O1 to JD-O3).

Further insights into the effects of treatment on the formation of DBPs can be gained by comparison of the removal of DOC and DBP precursors (*i.e.* the portion of DOC that leads to the formation of DBPs, quantified by DBP concentrations produced during FP experiments) (Table S12, Appendix A SI9) and the change in the formation of DBPs per unit DOC (Table 4). For the conventional treatment train, a higher proportion of TOX precursors (*i.e.* TOX FP) and HAN precursors were removed than bulk DOC for both chlorination and chloramination. Similar removals of DOC and THM FP were observed in chlorination, but there was no clear trend in the chloramination experiments. However, the increase in the concentration of bromide, an inorganic precursor to THMs, increased the concentration of brominated THMs. While HNMs and HAMs were not detected in the chlorinated samples, conventional treatment removed a lower proportion of HNM precursors compared to DOC, and was not effective in removing HAM FP for chloramination experiments.

For the O_3 + BAC treatments, the proportions of TOX and THM precursor removal were both higher than the DOC removal for both disinfection strategies, however, HAN FP removal was only better than DOC removal for chloramination experiments. In contrast, HAN FP from chlorination increased following O_3 + BAC treatment. Similar to conventional treatment, a lower proportion of HNM precursors were removed compared to DOC removal for chloramination experiments, while a greater removal of HAM FP than DOC was observed. There was no clear trend in the formation and specific yields of *N*-nitrosamines from laboratory chlorination and chloramination following different treatments (Table 4). In chlorination experiments, *N*-nitrosoethylmethylamine (NEMA) was the main species detected and the concentrations of *N*-nitrosamines increased following conventional treatment, but were consistently reduced with all O_3 + BAC treatments (Table 4, Appendix A SI6). In chloramination experiments, NDMA was the main species detected, and conventional treatment removed more *N*-nitrosamine precursors than O_3 + BAC, where an increase in the formation of *N*-nitrosamines was observed. It is possible that O_3 + BAC treatment may have produced *N*-nitrosamine precursors that react favourably with chloramine to form *N*-nitrosamines. Bond and Templeton (2011) have reported that ozonation prior to chloramination increased *N*-nitrosamine yield

from secondary amines, although Mitch et al. (2009) showed that ozonation prior to chloramination minimised the formation of NDMA.

In general, both treatment methods evaluated in this study achieved greater removal of DBP precursors than DOC, however the removal of DOC does not imply the removal of DBP precursors. Where DOC was removed but DBP formation was not, the treatment process may have removed mainly non-DBP precursors, leaving a higher proportion of DBP precursors. Differences in DOC removal and DBP precursor removal resulting from different treatment methods led to significant changes in DBP proportions in the disinfected waters (Fig. 3; Tables S8 and S9, Appendix A SI7). After water treatment (conventional with additional O_3 + BAC), the proportion of THMs contributing to TOX (10% for chlorination and 1.3% for chloramination) increased (12%–15% for chlorination and 7.2%–12% for chloramination). This suggests that some THM precursors were not well removed by treatment. For chloramination experiments, the proportion of halogenated N-DBPs contributing to TOX decreased from 0.20% to 0.06%–0.13% with treatment, indicating the removal of N-DBP precursors, especially HAN precursors. However, for chloramination experiments, the proportions of halogenated N-DBPs contributing to TOX increased from 1.1% to 1.5%–29%, supporting the hypothesis that monochloramine itself contributes a nitrogen source for N-DBP formation. Although the trends in *N*-nitrosamine formation were unclear, the treatment generally increased the contribution of *N*-nitrosamines to total N-DBPs in both chlorination (from 0.02% to 0.24%–1.1%) and chloramination (from 0.13% to 0.50%–0.90%) experiments, indicating that the treatment was not effective in removing *N*-nitrosamine precursors relative to other DBP precursors. The effectiveness of the O_3 + BAC treatment processes was also assessed using a scoring system that considered the removal of DOC and DBP precursors, as well as DBP formation (Appendix A SI10). This assessment suggested that the conventional treatment followed by O_3 + BAC treatment at JD-O3, using coconut-based GAC (Acticarb GC1200N 6 × 12 mesh), was most effective in reducing overall DBP formation (TOX, THMs, and N-DBPs), compared to O_3 + BAC treatment using the other activated carbon media. For the removal of N-DBPs specifically, conventional treatment followed by O_3 + BAC treatment at JD-O2, using coal-based GAC (Acticarb GA1000N 8 × 16 mesh), was most effective.

DBP additive toxicity was also calculated to evaluate the impact of water treatment on the toxicity of chlorinated and chloraminated waters (Table 5). Unlike the source water samples (Table 2), there was no correlation between DBP additive toxicity and the bromide concentration in these JD treated waters. The calculated overall toxicity of chlorinated and chloraminated JD waters generally decreased following treatment. There was one exception, however, where the toxicity increased by two orders of magnitude, caused by the unusually high concentration of DBAM measured in the chloraminated J-PF sample. As in the case of the source waters, the calculated toxicity of chlorinated JD waters was dominated by HANs (77%–96%), with THMs providing the second highest contribution (3%–23%). In chloraminated waters, the major contributor to toxicity shifted from HANs (70%) to the HAMs after treatment (77%–100%), reflecting the higher concentration of HAMs, and DBAM in particular, after both conventional treatment and O_3 + BAC. *N*-nitrosamines did not contribute more than 4% of overall additive toxicity in any sample, further highlighting the significance of HANs and HAMs in their contribution to the overall toxicity of chlorinated and chloraminated waters. Given the high concentration of bromide in this system, toxicity contributions from bromate are also possible. Previous studies of bromate in this water treatment plant showed that bromate was always less than 0.2 μg/L in the conventional water treatment system (Nottle, 2013), and thus at least 2 orders of magnitude lower than the Australian Drinking water Guideline of 20 μg/L (NHMRC-NRMMC, 2011). However, laboratory-based ozonation studies did indicate bromate could be formed above the guideline from JD waters (Nottle, 2013), and therefore could contribute to toxicity in the O_3 + BAC treated waters.

3. Conclusions

This is the first comprehensive study of the potential formation of 4 classes (30 species) of N-DBPs from the chlorination and chloramination of raw source waters incorporating organic matter characterisation and DBP toxicity assessment. The formation of N-DBPs could not be predicted by the routinely measured water quality parameters (*e.g.* UV_{254}, $SUVA_{254}$, DOC) and commonly measured DBPs (*e.g.* THMs). The formation of all N-DBPs except for HANs was more significant in chloraminated waters, consistent with studies previously reported for DBP formation and also those observed in previous studies of WA distribution systems. However, the DBPs measured in this study accounted for only a small portion of TOX in both chlorinated and chloraminated waters.

Both $SUVA_{254}$ and bromide concentration were important factors controlling the formation of TOX, THMs and HANs, although the influence of $SUVA_{254}$ and bromide could not be explicitly distinguished. While the role of aromatic organic compounds in THM and TOX formation has been previously identified, it is likely that, in this study, the bromide concentration had a more important role in DBP formation. This was reflected in the increased formation of brominated DBPs with increasing bromide concentration for all halogenated DBPs measured, in all waters studied. The low correlation between HNM, HAM, and *N*-nitrosamine formation and $SUVA_{254}$ suggests that the precursors of these N-DBPs are not from aromatic organic compounds within NOM. Instead, the moderately positive correlations between HNM, HAM, and *N*-nitrosamine formation and DON, suggested that DON is an important precursor for these N-DBP classes, especially in chlorination experiments.

N-DBPs were major contributors to the calculated additive toxicity (>80%) of both chlorinated and chloraminated waters. In particular, brominated HANs were the major contributor for all source waters. The strong correlation between bromide concentration and the overall DBP additive toxicity for both chlorinated and chloraminated source waters demonstrated the impact of bromide on the toxicological properties of disinfected waters. Despite their high toxicity, *N*-nitrosamines only contributed significantly to toxicity when concentrations of brominated HANs, and the overall additive toxicity, were low. It must be noted, however, that the additive toxicities calculated only indicate the relative health importance of the

Table 5 – DBP additive toxicities [a] in chlorinated and chloraminated JD groundwater samples.

DBP class	Additive toxicity				
	JD-raw	JD-PF	JD-O1	JD-O2	JD-O3
Chlorination					
THMs	2.23×10^{-4}	9.35×10^{-5}	8.83×10^{-5}	6.48×10^{-5}	8.25×10^{-5}
HANs	6.24×10^{-3}	3.14×10^{-4}	1.67×10^{-3}	7.06×10^{-4}	9.40×10^{-4}
HNMs	n.d.	n.d.	n.d.	n.d.	n.d.
HAMs	1.13×10^{-7}	n.d.	n.d.	n.d.	n.d.
Nitrosamines	5.19×10^{-7}	6.52×10^{-7}	4.22×10^{-7}	5.3×10^{-7}	5.30×10^{-7}
All DBPs	6.47×10^{-3}	4.08×10^{-4}	1.75×10^{-3}	7.71×10^{-4}	1.02×10^{-3}
Chloramination					
THMs	4.93×10^{-6}	1.26×10^{-5}	3.23×10^{-6}	7.6×10^{-6}	4.33×10^{-6}
HANs	3.72×10^{-4}	n.d.	9.07×10^{-5}	1.64×10^{-5}	6.15×10^{-5}
HNMs	1.60×10^{-6}	n.d.	n.d.	n.d.	n.d.
HAMs	1.38×10^{-4}	1.05×10^{-2}	3.91×10^{-4}	3.90×10^{-4}	3.20×10^{-4}
Nitrosamines	1.17×10^{-5}	2.12×10^{-7}	1.17×10^{-5}	2.26×10^{-7}	1.44×10^{-5}
All DBPs	5.28×10^{-4}	1.05×10^{-2}	4.97×10^{-4}	4.14×10^{-4}	4.00×10^{-4}

n.d.: not detected.
[a] DBP additive toxicity was calculated according to the method published in Zeng et al. (2016).

DBPs measured; and that the calculated additive toxicities only refer to potential health risks, rather than absolute risks, since the data used to calculate these toxicities were obtained from cell-based assays rather than animal studies or epidemiological studies.

Evaluation of the influence of conventional and O_3 + BAC treatment methods on DBP formation and precursors showed that, while conventional treatment process (coagulation-flocculation-clarification-filtration) removed the majority of DOC in the source water, O_3 + BAC altered the reactivity of the organic carbon, leading to increased DBP formation for some classes. Additionally, there was no net removal of bromide during either conventional or O_3 + BAC treatment, and the increased bromide to DOC ratio in treated waters led to dramatic increases in bromine incorporation in halogenated DBPs. Thus, the removal of DOC does not imply the same removal of DBP precursors, particularly if bromide concentrations remain high. Overall, the total N-DBP formation increased after O_3 + BAC treatment for both chloramination and chlorination experiments, suggesting that O_3 + BAC was not effective in removing N-DBP precursors. While total N-DBP formation was higher for chloraminated samples compared to chlorinated samples, the overall additive toxicity of chloraminated samples remained lower because HAN formation was reduced, while the concentrations of less toxic HAMs increased.

The results of this study highlight the fact that the occurrence and formation of N-DBPs should be investigated on a case-by-case basis, especially where advanced water treatment methods are being considered to minimise their formation in drinking waters, and where chloramination is used for final disinfection.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.06.028.

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