DISINFECTION BY-PRODUCTS

A case study of occurrence of non-regulated disinfection by-products from the Capalaba region's distribution system

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Summary

A survey of disinfection by-product (DBP) occurrence was conducted at the Capalaba Water Treatment Plant (WTP) in Brisbane and at 19 sampling points of the distribution system for six months through spring-summer 2011. In addition to currently regulated DBPs including N-nitrosodimethylamine (NDMA), DBPs that were reported as high priority due to potential toxicity were studied. These priority DBPs included five iodinated trihalomethanes (THMs), four haloacetonitriles (HANs), two haloketones (HK), chloronitromethane and chloral hydrate (CH). Results showed that all the measured regulated DBPs, including CH, were below the *Australian Drinking Water Guidelines* (ADWG) recommendations.

THM speciation followed the order trichloromethane (TCM) > bromodichloromethane (BDCM) > dibromochloromethane (DBCM) > tribromomethane (TBM) in waters provided by the Capalaba WTP. The order was DBCM>BCDM>TBM>TCM for waters provided by the North Stradbroke Island (NSI) WTP as a result of different dissolved organic carbon/bromide (DOC/Br) ratios. HANs were measured at the WTP and across the distribution system at significant concentrations, but still lower than the World Health Organization (WHO) recommendations in the case of dichloroacetonitrile and dibromoacetonitrile. Speciation of brominated and chlorinated HANs followed the trends observed for THMs. The formation of iodinated-THMs was low, in agreement with the iodide concentration measured. NDMA was not detected above the limit of detection (5 ng/L). NDMA formation potential of source water at the Capalaba WTP was 11.4 ± 3.4 ng/L, which is well below the ADWG (i.e., 100 ng/L).

Keywords

Chlorine, distribution system, emerging DBPs.

Introduction

Naturally occurring organic matter, which is present in raw waters, reacts with disinfectants to form disinfection by-products (DBPs). Formation of DBPs in drinking water is of concern as some have been linked to potential health effects (Richardson et al., 2008). Chlorine reacts with natural organic matter (NOM) and/or anthropogenic compounds to produce a mixture of DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs). Regulated THMs include trichloromethane, bromodichloromethane, dibromochloromethane and bromoform. Total THMs (tTHMs) refers to the sum of these four compounds. The USEPA regulates tTHMs at 80 µg/L (USEPA, 1998), while the value for the *Australian Drinking Water Guidelines* (ADWG) is 250 µg/L (NHMRC, 2011).

There are 15 HAAs that can be formed in the presence of chlorine, bromide and iodide. The most common are dichloroacetic acid (Cl_2AA) and trichloroacetic acid (Cl_3AA). Other species, found generally at lower levels, are bromochloroacetic acid (BrClAA), dibromoacetic acid (Br_2AA), monochloroacetic acid (ClAA) and monobromoacetic acid (BrAA) as well as additional iodine-containing counterparts. In the US, the sum of Cl_2AA, Cl_3AA, Br_2AA, ClAA and BrAA is commonly denoted as HAA5 and is currently regulated at 60 µg/L (USEPA, 1998). In Australia, only ClAA, Cl_2AA and Cl_3AA are regulated, at 150, 100 and 100 µg/L, respectively (NHMRC, 2011). While the USEPA drinking water standards for tTHMs and HAAs are numerically lower than the Australian drinking water guideline values, compliance in the US is defined on the basis of a running annual average of quarterly averages of all samples, whereas compliance is based on single exceedances in Australia.

Recently, Australia has included N-nitrosodimethylamine (NDMA) in the ADWG at the World Health Organization (WHO) guideline value of 100 ng/L (NHMRC, 2011; WHO, 2011). Other DBPs that may be generated at lower concentrations are haloacetonitriles (HANs), halogenated furanones, halonitromethanes (HNM), cyanogen halides, haloketones (HK), haloaldehydes and halogenated phenols, among others. However, the concentration of the halogenated DBPs identified to date account for less than 50% of the total organic halogens (TOX) present in a chlorinated water (Reckhow and Singer, 1984; Buffle et al., 2004).

Nitrogen-containing DBPs (N-DBPs) such as HANs and N-nitrosamines are suspected to be more toxic than carbon-based DBPs (Plewa et al., 2004; Muellner et al., 2007; Plewa et al., 2007). The higher toxicity of N-DBPs have already raised concerns, with regulators in Australia including NDMA at 100 ng/L, which is three orders of magnitude lower than the values used for more conventional DBPs such as tTHMs (tTHMs 250 µg/L). HANs are currently not included in the ADWG; however, some of them are already included in the recycling water guidelines, with values as low as 0.7 µg/L for bromochloroacetonitrile (QPC, 2005). Moreover, N-DBP precursors are less amenable to conventional drinking water treatment processes than most precursors for carbon-based DBPs, due to their hydrophilic characteristics (Bond et al., 2011).

Conventional water treatment systems are designed to treat potentially contaminated source water, in order to prevent the potential spread of waterborne disease-causing micro-organisms and reduce potable water problems related to NOM, such as undesirable colour, odour, taste and formation of DBPs. Such treatment systems typically consist of source water intake/screening, coagulation, flocculation, sedimentation, rapid sand filtration and disinfection processes (Kameya et al., 1997). Coagulation changes the composition of organic matter by preferentially removing more oxidised NOM compounds, leaving compounds with a higher tendency to form chlorine-generated N-DBPs such as HANs (Xiao et al., 2010).

Nitrogen-containing DBPs have been measured mainly in the United States (US), Canada and Europe (Richardson *et al.*, 2007). Simpson and Hayes sampled 16 drinking waters from around Australia and measured the sum of four HANs expressed as 4HAN, chloropicrin and cyanogen chloride (Simpson and Hayes, 1998). They found values up to 36 µg/L of 4HAN in different regions of Australia compared to the median and maximum levels of 3 and 14 µg/L found in a 2000–2002 US survey (Weinberg *et al.*, 2002; Krasner *et al.*, 2006). In a 2006–2007 US survey, median values for the sum of 4HAN was slightly higher at 4 µg/L (Mitch *et al.*, 2009).

In our previous work, we measured the DBP formation potential at three WTPs in Brisbane and found the highest DBP formation from Capalaba source water (Farré *et al.*, 2011). Therefore, we selected this region for further evaluation. In this paper we present the concentration of DBPs at Capalaba WTP (Brisbane) and its distribution system, which also includes water from North Stradbroke Island (NSI).

Methodology

Samples were taken at Capalaba WTP and from the distribution system (Figure 1) during five sampling events in spring-summer 2011.

The sampling dates were 5/9/2011, 3/10/2011, 7/11/2011, 21/11/2011 and 6/12/2011. Samples were taken headspace free, in acid-washed glass containers with Teflon lids. Ascorbic acid was used to quench the chlorine and to protect the present DBPs. Samples were shipped to The University of Queensland (UQ), with volatile DBPs analysed within 24 hours. The following

Figure 1. Sampling points selected for the study.

NSI = North Stradbroke Island. Green = Capalaba WTP source water. Red = NSI WTP source water. Purple = Alexandra Hill Reservoir (Capalaba + NSI). Blue = Capalaba + Alexandra Hill Reservoir. White arrow represents water from Capalaba to Alexandra Hill Reservoir *(Courtesy of Allconnex Water).*

DBPs were extracted by liquid-liquid microextraction and analysed by gas chromatography with electron capture detection (GC/ECD): trichloromethane (TCM); bromodichloromethane (BDCM); dibromochloromethane (DBCM); tribromomethane (TBM); dichloroiodomethane (DCIM); bromochloroiodomethane (BCIM); dibromoiodomethane (DBIM); chlorodiiodomethane (CDIM); bromodiiodomethane (BDIM); trichloroacetonitrile (TCAN); dichloroacetonitrile (DCAN); bromochloroacetonitrile (BCAN); dibromoacetonitrile (DBAN); chloral hydrate (CH); trichloronitromethane (TCNM); 1,1-dichloropropanone (1,1-DCP); and 1,1,1-trichloropropanone (1,1,1-TCP). Additional analyses such as total organic carbon (TOC), SUVA, bromide and iodide were done. NDMA was extracted at UQ by means of solid phase extraction and concentration under nitrogen and samples were taken to QHFSS for analysis by gas chromatography coupled to mass spectrometry (GC/MS) with chemical ionisation with ammonia gas.

Results

Table 1 shows TOC, bromide, dissolved and organic nitrogen (DON) values and the standard deviation for the sampling points selected for this study and Capalaba WTP. Samples have been divided according to the source water used. Samples M16 and M17 provide water from Capalaba WTP and Alexandra Hill Reservoir, which is a mix of Capalaba and NSI water. Hence, a higher proportion of Capalaba water is expected for these sites in comparison to sites M19–M33, which supply water from Alexandra Hill Reservoir without further blending. Maximum average TOC values were around 5–6 mg/L and were found in sampling points with a higher percentage of water from Capalaba WTP, while lower values were found in sampling points providing water from NSI. Bromide concentration ranged between 0.025 and 0.07 mg/L across the samples. DON was clearly higher in Capalaba water in comparison to NSI.

THMs in conjunction with HAAs are the most prevalent DBPs in drinking water and are formed as a result of the reaction between chlorine and NOM. Figure 2 shows the mean concentrations of tTHMs found in Capalaba WTP and the distribution system.

In all instances, tTHM values were lower than the ADWG value of 250 µg/L. Elevated values were found in M8–M17 which correspond to sampling points providing water from Capalaba WTP. On the other hand, the remaining sampling points provided water with a high contribution of NSI-treated water. Average concentrations of tTHMs at Capalaba WTP were lower than at M8, M11, M13, M14 and M16, which evidenced the ability of THMs to increase during distribution within the system, mainly as a result of hydrolysis of other DBPs (Nikolaou *et al.*, 2001). Sampling points providing water from Capalaba showed a distribution of TCM>BDCM>DBCM>TBM, which is common speciation in drinking water with a high concentration of organic carbon and low concentration of bromide. The speciation of THMs measured in sampling points providing water from NSI was DBCM>BCDM>TBM>TCM as a result of the presence of bromide in low organic carbon waters (< 2 mg/L). The rate constant of bromide with HOCl to generate HOBr is 1.5×10^3 1/M·s (Kumar and Margerum, 1987) and the rate constant of THM formation is in the range of 0.01 and 0.03 1/M·s (Gallard and Von Gunten, 2002). It is known that, once formed, hypobromous acid reacts about 10 times faster than chlorine with NOM. The reason is that the activities of electrophilic substitution for electron release to stabilise a carbocation are more favourable for the Br atom due to its higher electron density and smaller bond strength relative to the Cl atom (Westerhoff *et al.*, 2004). Hence, the formation of Br-DBPs is limited by the initial Br concentration, whereas the
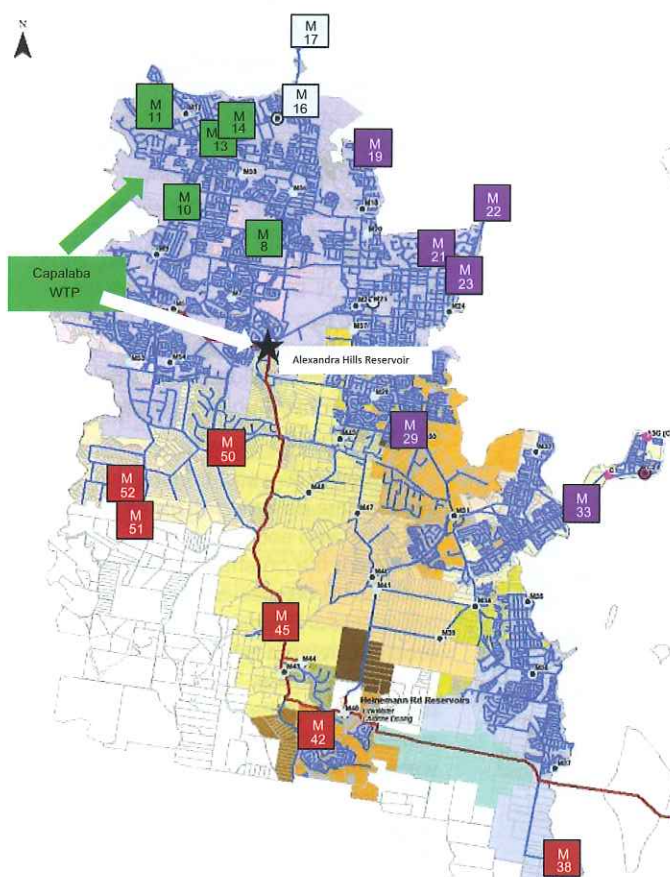
Table 1. Water characterisation during the sampling campaign in the Capalaba distribution system. n = number of samples, TOC = total organic carbon, DON = dissolved organic nitrogen, SUVA = specific UV absorbance, Cap = Capalaba WTP, NSI = North Stradbroke Island WTP.

Sampling point	n	Source water	TOC mg/L	St dev	Br- mg/L	St dev	DON mg/L	St dev
M8	5	Cap	3.83	0.79	0.025	0.004	0.29	0.29
M10	5	Cap	2.31	2.07	0.036	0.007	0.21	0.08
M11	4	Cap	4.93	0.72	0.051	0.006	0.29	0.15
M13	5	Cap	4.49	1.18	0.038	0.006	0.36	0.04
M14	4	Cap	4.07	1.42	0.040	0.005	0.29	0.08
M16	5	Cap + NSI (via Alexandra Hills res)	4.92	2.25	0.041	0.007	0.33	0.26
M17	4	Cap + NSI (via Alexandra Hills res)	2.93	0.64	0.060	0.008	0.27	0.13
M19	5	Alexandra Hills res (Cap + NSI)	1.67	0.63	0.030	0.005	0.15	0.12
M21	4	Alexandra Hills res (Cap + NSI)	2.46	1.81	0.030	0.005	0.11	0.10
M22	2	Alexandra Hills res (Cap + NSI)	1.07	0.34	0.027	0.005	0.14	0.07
M23	4	Alexandra Hills res (Cap + NSI)	2.10	2.48	0.043	0.007	0.20	0.18
M29	4	Alexandra Hills res (Cap + NSI)	1.00	1.07	0.066	0.003	0.11	0.04
M33	2	Alexandra Hills res (Cap + NSI)	0.55	0.34	0.060	0.002	0.11	0.01
M38	3	NSI	1.97	2.18	0.065	0.009	0.10	0.03
M42	3	NSI	1.89	2.56	0.070	0.003	0.09	0.12
M45	3	NSI	0.64	0.50	0.066	0.001	0.14	0.11
M50	4	NSI	0.46	0.42	0.064	0.004	0.08	0.10
M51	5	NSI	0.75	0.47	0.059	0.006	0.15	0.09
M52	3	NSI	1.21	0.34	0.061	0.002	0.13	0.11
Cap	4		5.99	0.97	0.053	0.007	0.32	0.11
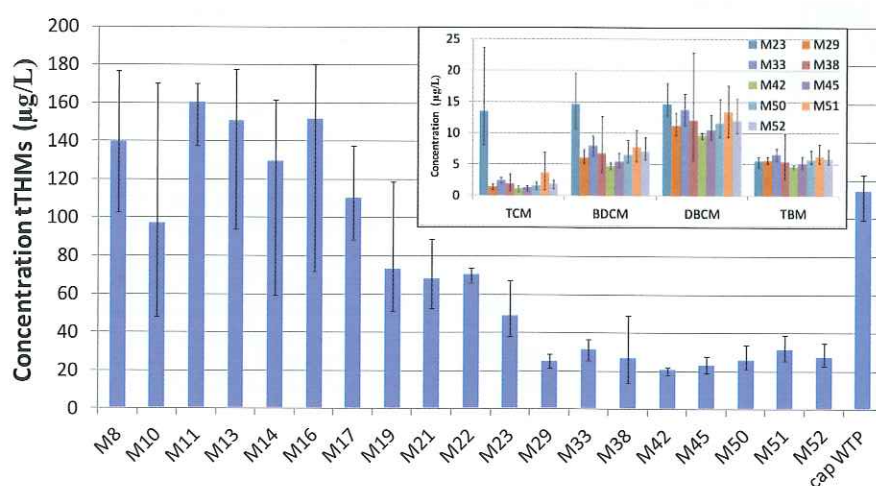
Figure 2. Average concentration and range of tTHMs in Capalaba WTP and distribution system. Inset shows the THMs speciation in waters from NSI.

Cl-DBPs would be limited by the organic matter concentration. Figure 2 shows the average concentration of THMs in the waters with a high contribution from NSI.

Figure 3 shows the average concentration of the four analysed HANs. In agreement with Bougeard and co-authors (2010), all four analysed HANs were detected in all waters and their concentrations were typically an order of magnitude lower than the concentration of THMs. Also, the bromine/chlorine speciation was different between the sampling points providing water mainly from Capalaba WTP or NSI WTP as a result of the different concentration of TOC. Maximum concentrations measured corresponded to DCAN. Dihalogenated HANs are reported to be more stable than the trihalogenated HANs (Peters et al., 1990). In addition, TCAN can undergo base-catalysed hydrolysis at pH higher than 5.5, which is the likely explanation as to why it was rarely detected in this sampling campaign, as the pH of all the samples was 7±0.4 (Croue and Reckhow, 1989). Although HANs are not included in the ADWG, the WHO has recommended the concentration of DCAN and DBAN to be 20 and 70 µg/L, respectively (WHO, 2011).

Besides THMs and HAAs, CH is the next most prevalent DBP in chlorinated drinking water. Figure 4 shows the average concentration of CH also in conjunction with TCNM and two HKs.

At almost all the sampling points providing water from Capalaba WTP, concentration of CH was measured above 10 µg/L. Dabrowska and Nawrocki (2009) studied the effect of contact time on the formation of CH. They observed that the reaction of chlorine with organic matter takes place as long as chlorine is available in the water due to the different precursors involved in these reactions. Thus, the concentration of CH may continuously increase in the water supply system. CH has been previously studied, but the appearance of CH in drinking water is not well understood and causes many controversies (Goslan et al., 2009). Trehy et al. (1986) reported that amino acids are potential precursors of CH and suggested that the precursors for TCM and CH are different. According to Ueno et al. (1995), nitrogen compounds and amino acids produced CH in the chlorination process.

TCNM and 1,1-DCP concentrations were low in all instances, while 1,1,1-TCP was found at concentrations up to 12 µg/L in the waters coming from Capalaba WTP. The differences in the formation of 1,1-DCP and 1,1,1-TCP can be partially explained by a simplified
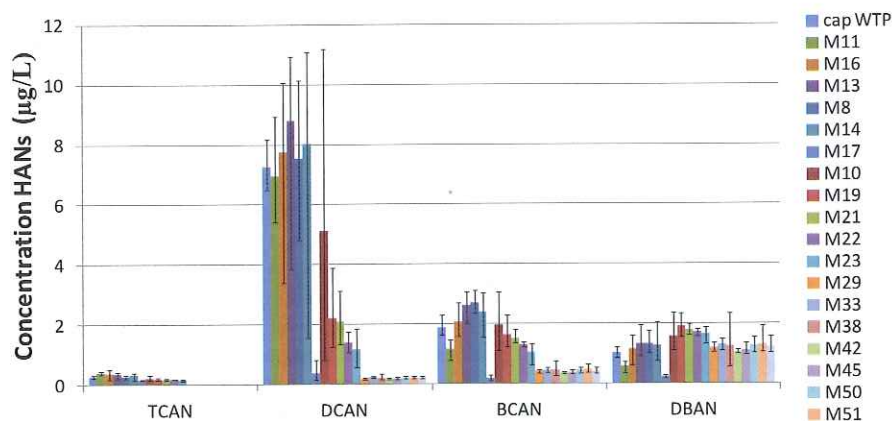
Figure 3. Average concentration and range of HANs in Capalaba WTP and distribution system.
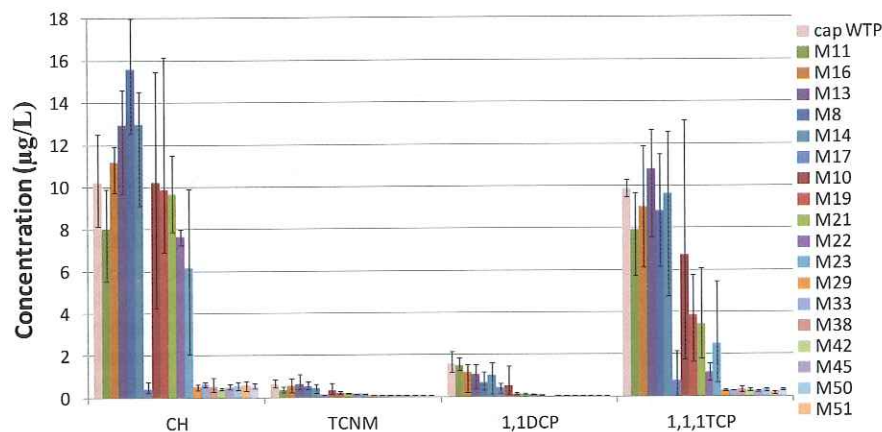

Figure 4. Average concentration and range of CH, TCNM, 1,1-DCP and 1,1,1-TCP in Capalaba WTP and distribution system.

model developed by Reckhow and Singer (1984). In their model, chlorination of fulvic acid solutions led to the formation of intermediate by-products, such as 1,1-DCP, that could be further oxidised by chlorine to 1,1,1-TCP. This model reveals that further chlorine attack and hydrolysis are essential for the formation of 1,1,1-TCP.

Five iodinated-THMs (I-THMs) were also measured in this study. We did not find I-THMs above 3.5 µg/L, which is in concurrence with the measurements of iodide in the samples that were, in all instances, below the 0.01 mg/L limit of detection (LOD). Similarly, NDMA was not detected above the 5 ng/L LOD across the distribution system. NDMA formation potential of source water at the Capalaba WTP was 11.4 ± 3.4 ng/L (n=3), which is also well below the ADWG value (i.e., 100 ng/L).

Conclusions

All regulated DBPs were measured below ADWG values in all analysed samples across the Capalaba region.

- THM speciation followed the order TCM>BDCM>DBCM>TBM in sampling points providing water from Capalaba and DBCM>BCDM>TBM>TCM in

waters blended with NSI water as a result of different DOC/Br ratios.

- HANs were measured at relatively high concentrations for locations serviced primarily by Capalaba WTP. Even though they were measured below WHO limits, we recommend investigating possibilities to control the formation of HANs at the drinking WTP as they are suspected to be more toxic than carbon-based regulated DBPs.

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technical features

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