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Occurrence, formation and persistence of halobenzoquinones: A case study on 2, 6 -dichloro-1, 4 -benzoquinone

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Occurrence, formation and persistence of halobenzoquinones:

A case study on 2, 6 -dichloro-1, 4 -benzoquinone

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Massachusetts in partial fulfillment of the requirements for the degree of

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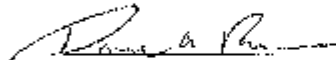
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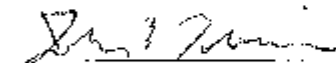
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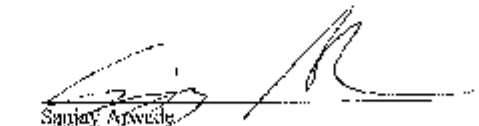
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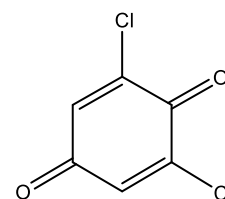

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ABSTRACT

Halobenzoquinones (HBQs) constitute an emerging class of potentially carcinogenic disinfection by-products (DBPs). Given that HBQs are not measured in routine analysis of drinking water, there is little data on their occurrence in the USA. The presence of 2, 6-dichloro-1, 4-benzoquinone (2, 6-DCBQ) in US drinking water facilities was investigated in 8 utilities to provide an initial assessment of occurrence and fate in relation to the regulated DBPs. Point of entry (POE) and distribution system (DS) samples with DCBQ concentrations greater than the 90th percentile values were from treatment plants that used free chlorine. Across distribution systems, DCBQ exhibited decreasing concentrations with water age whereas trihalomethane (THM) concentrations increased with water age. In an effort to better understand the source of DBP precursors, controlled laboratory experiments were conducted to examine the formation of DCBQ from chlorination and chloramination of specific classes of lignin model compounds namely p-hydroxyl phenols, vanillyn, syringyl and cinnamyl phenols, poly phenols and alkoxy groups. DCBQ yields from chlorination depended on the type and position of the substituents and potential intermediates and varied between n.d.-0.8 percent while chloramination did not result in DCBQ formation. Chlorination of p-hydroxyl phenols produced the highest DCBQ yield for the reaction period considered (6 h). To address the apparent loss of DCBQ in full-scale systems, the impact of different pHs on DCBQ degradation at ambient temperature was investigated and modeled. DCBQ remained relatively stable below pH 7 while the degradation rate above this pH was determined to be first order in $[\text{OH}^-]$ with a second order rate constant of $156 \text{ M}^{-1} \text{ s}^{-1}$.



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1. Introduction

Modern drinking water treatment processes have been successful in minimizing health hazards. Disinfection using oxidants like chlorine, chloramine, chlorine dioxide, ozone and their combinations reduces risks of water-borne disease outbreaks. Reactions between disinfectants and organic compounds in water (natural organic matter (NOM), anthropogenic organics, algal and effluent organic matter) and/or inorganic substances (bromide and iodide) produce diverse groups of undesired compounds called disinfection by-products (DBPs). Of the ~ 600 DBPs that have been identified in treated drinking water (Boorman et al., 1999; Richardson, 1998), trihalomethanes (THMs) and halo acetic acids (HAAs) constitute about 25 % of the halogenated DBPs (Krasner et al., 2006) and are the only ones regulated by the US Environmental Protection Agency (EPA). Given the need for regulation of identified DBPs that have adverse human and ecological health effects (Cantor, 1997; Cantor et al., 1999; Bull et al., 2011; Doyle et al., 1997; Richardson et al., 2007), knowledge of their sources and behavior in public water systems is essential.

Halobenzoquinones (HBQs) are DBPs (Qin et al., 2010; Zhao et al., 2010) that have been given high priority due to their suspected bladder carcinogenicity (Bull et al., 2006). They contain highly polar carbonyl groups and resemble aromatic quinones in which hydrogen atoms are replaced by halogens. Zhao et al., (2010) detected HBQs in chlorinated waters at 0.5-165 ng/L. Subsequently, Zhao et al., (2012) observed high occurrence frequencies (9/9 utilities) of 2,6-dichloro 1,4-benzoquinone (DCBQ) among other HBQs analyzed in effluent samples from US and Canadian utilities. In these samples, DCBQ was found at 4.5-274.5 ng/L while other HBQs like 2,6-dichloro-3-methyl-1,4-benzoquinone (DCMBQ), 2,6-dibromo-1,4-benzoquinone (DBBQ) and 2,3,6-trichloro-1,4-benzoquinone (TCBQ) were detected below 37.9 ng/L. Samples from distribution systems were not analyzed in this study. However, Wang et al., (2014) observed a decrease in HBQs with increasing distances from WTPs across

Canadian distribution systems. There is a clear need for similar studies in US utilities considering there is almost no data regarding HBQ occurrence in distribution systems. Also, none of the published research investigated the fate of HBQs relative to the regulated DBPs. Despite the suggested higher toxicity levels of brominated benzoquinones than chlorinated benzoquinones (Anichina et al., 2010; Lai et al., 2011), DCBQ needs more focus due to its relatively higher concentrations. Therefore, additional data on DCBQ levels in US utilities are required to characterize its actual and relative spatial variation.

DCBQ exposure assessments by measurements at the plant effluent can be misleading due to degradation in distribution systems. HBQs have been found to be unstable with 80 % degradation at typical UV doses used in water treatment plants (Qian et al., 2013). The end products identified included hydroxylated-HBQs (OH-HBQs), halo-benzenetriols and monohalogenated benzoquinones. However, this was more relevant to plants using UV irradiation after chlorination and can be considered while sampling prior to the plant effluent and not the distribution system. Following this, Wang et al. (2014) observed an increase in OH-HBQs with decrease in HBQs across the distribution system (DS) and confirmed the existence of OH-HBQs as stable transformation products. Despite the comprehensive literature, published research has reported only the degradation of DCBQ with no kinetic analysis or when there have been time course studies of DCBQ conversion to OH-DCBQ, the focus was primarily synthesis and confirmation of OH-HBQs, whereby the experimental conditions were not characteristic of most drinking water systems (eg., pH= 4.5, T=4 °C) (Wang et al., 2014) . No prior research has systematically studied and modeled DCBQ degradation at ambient temperature over a range of pHs. These effects are not only significant in understanding the fate of DCBQ in DS but also important for identifying suitable monitoring locations, assessing exposure, developing approaches to minimizing DCBQ formation and establishing sample preservation protocols for accurate analysis.

The characteristics and concentration of natural organic matter (NOM) influence a water's propensity to form DBPs. Thurman., (1985) proposed that NOM contains short-chain acids and neutral molecules (hydroxyl, ether, ketone, ester, aldehyde and lactone). NOM which is a complex mixture of fractions that are hydrophilic (proteins, carbohydrates, carboxylic acids, amino acids, amino sugars) and hydrophobic (humic and fulvic acids) (Croue et al., 2000) is measured as dissolved organic carbon (DOC) (Volk et al., 2002). Croue et al., (2000) confirmed that humic substances in NOM contribute 75 % of DOC in natural waters and 85 % to DBP precursors, while Ertel et al., (1984) proposed that they are primarily composed of lignin derived aromatics. Researchers have established a link between formation of regulated DBPs and lignin precursors, by using different lignin and humic model compounds as surrogates of NOM (Boyce and Hornig, 1983; Conrad and Huck, 1996; Gallard and von Gunten, 2002; Hua et al., 2014; Larson and Rockwell, 1979). In fact lignin phenols have been proposed as important trichloroacetic acid (TCAA) precursors (Hua and Reckhow, 2007). However, there is lack of quantitative investigation on formation of specific unregulated DBPs of concern from these lignin groups. We hypothesize that lignin phenols may be potential DCBQ precursors because: (1) phenol is a known HBQ precursor (Heasley et al., 2004) and its chlorination results in maximum DCBQ production in 36 h (Zhao et al., 2012); (2) NOM fractions containing smaller molecular weight humic substances and LMW neutral organics including phenols contribute to DCBQ formation (Diemert et al., 2013); (3) mechanistic deductive reasoning points to phenolic NOM substructures as likely precursors to halogenated quinones (Bull et al., 2006).

The objectives of this study were (1) to evaluate DCBQ occurrence and fate relative to the THMs; (2) to examine its formation from specific NOM surrogates; (3) to model DCBQ loss at drinking water pHs. Samples were collected from 8 drinking water treatment plants (WTPs) using different treatment processes and analyzed for DCBQ. Raw water parameters,

water ages and treatment processes were considered for overall characterization of DCBQ occurrence. Controlled DCBQ formation tests were conducted on selected lignin groups using chlorination and chloramination. Identifying major precursors and understanding the chemistry of DCBQ formation can help better manage precursors in source waters. Time course studies conducted on DCBQ at different pHs will contribute to predicting its half-life in treated waters.

2. Experimental methods

2.1. Chemicals

2, 6-dichloro-1, 4-benzoquinone was obtained from Sigma-Aldrich (St. Louis, MO). Optima methanol (LC/MS grade) and Optima formic acid (FA, LC/MS grade) were purchased from Fisher Scientific (Fair Lawn, NJ). Formic acid (FA, ACS grade) was purchased from Alfa Aesar (Ward Hill, MA). For chlorination experiments sodium hypochlorite solution (laboratory grade, 5.65-6%) from Fisher Scientific and DPD indicator, phosphate buffer and ferrous ammonium sulfate (0.00282M) from Ricca Chemical Company (Arlington, TX) were used. The chemical structures of lignin model compounds used in this study are presented in Figure 1. Most of these compounds (p-hydroxyl, vanillin, syringyl and cinnamyl phenols) have been reported as end products from CuO oxidation of aquatic organic matter (Hedges and Ertel, 1982; Thevenot et al., 2010). However, compounds with excess and no phenolic group were also included. Most lignin model compounds were purchased from Sigma-Aldrich (St. Louis, MO). Gallic acid was obtained from Fisher Scientific. Hydroquinone and catechol were purchased from Acros Organics (NJ, USA).

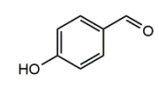
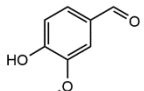
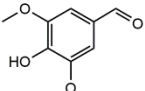
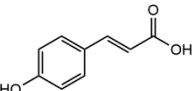
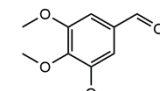
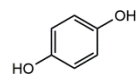
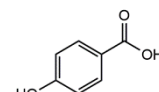
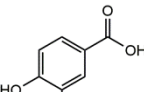
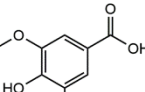
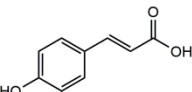
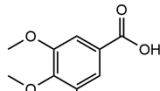
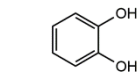
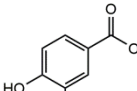
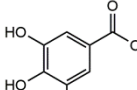
	p-hydroxy phenols	Vanillyl phenols	Syringyl phenols	Cinnamyl phenols	Alkoxy monomers	Polyphenols
Aldehydes	 p-hydroxybenzaldehyde	 Vanillin	 Syringaldehyde	 p-coumaric acid	 3,4,5-trimethoxybenzaldehyde	 Hydroquinone
Acids	 p-hydroxybenzoic acid	 Vanillic acid	 Syringic acid	 Ferulic acid	 3,4,5-triethoxybenzoic acid	 Catechol
					 3,4-dihydroxybenzoic acid	 Gallic acid

Figure 1: Chemical structures of lignin compounds.

2.2. Sampling

Sample sets included raw water, treated water and distributed water collected from eight different water treatment plants in the USA. The sites sampled in this study targeted treated water at point of entry (POE) into distribution systems. After evaluation of different sample preservatives (Figure S1), 0.25 % formic acid was used to stabilize DCBQ in all samples immediately after collection. WTP 1, 2, 3, 5 and 8 used chlorination and conversion to chloramines prior to distribution. WTP 6 and 7 used chlorination while WTP 4 used chlorine dioxide for primary disinfection and free chlorine as secondary. The detailed treatment processes have been presented in Table S1a and S1b. The average retention time in distribution systems based on a survey of over 800 U.S utilities is 1.3 days with a maximum of 3.0 days (Water industry database, AWWA and AWWARF 1991 (EPA, 2002)). Distributed waters for WTPs 1, 2 and 4 were sampled from short (< 3 days) and long (> 3 days) water age locations while for WTP 3, samples were collected only from short water age locations. The

different raw water quality parameters have been summarized in Table 1. Total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were determined with a TOC-V_{CPH} total organic carbon analyzer (Shimadzu Corp., Kyoto, Japan). Ultraviolet absorbances at 254 nm (UV₂₅₄) were measured with an Agilent 8453 UV-Vis spectrophotometer (Agilent, Santa Clara, CA). For DOC and UV₂₅₄ measurements, samples were filtered with glass fiber filters (GF/C, 0.7 μm) (Whatman, Clifton, NJ). Specific ultraviolet absorbance (SUVA₂₅₄) was calculated from UV absorbance at 254 nm (UV₂₅₄, m⁻¹) divided by the dissolved organic carbon (DOC, mg/L). pHs were measured using Expandable Ion analyzer EA 940 (Orion Research, Beverly, MA). Raw waters from WTP 5 and 8 were low in humic content with SUVA₂₅₄ values below 2 L/mg m⁻¹. The TOC and DOC for source waters of WTPs 5, 7 and 8 were over 5 mg/L which is greater than other WTPs. The difference between TOC and DOC for the source waters was consistently between 0.7-1 mg/L with DOC being 75-122 % of TOC. The pH and temperature of treated waters ranged from 7-8.7 and 4-26 °C respectively while the residuals were between 0.8-2.8 mg Cl₂/L. Samples in pre-cleaned 1-L glass bottles were transported in coolers with ice packs and stored at 4 °C prior to analysis. DCBQ analysis was carried out in less than a week after collection. For THM analysis, samples were transported and stored at 4 °C in 1-L borosilicate glass containers and analyzed within two weeks. Ascorbic acid at 10 mg/L was used for preserving THMs.

Table 1: Water quality parameters for WTP 1-8

WTP	Sampling date	TOC (mg/L)	DOC (mg/L)	UV ₂₅₄ (cm ⁻¹)	SUVA ₂₅₄ (L/mg m ⁻¹)	Treated water pH	Treated water T (°C)	Disinfectant Residual (mg Cl ₂ /L)
1	02/2014	2.49	2.21	0.11	0.14	7.20	7	2.1
	03/2014	1.66	1.41	0.05	3.83	7.14	8	2.25
	04/2014	1.94	1.83	0.069	3.77	7.26	16	2.05
	05/2014	4.41	3.82	0.21	5.52	7.23	23	2.2
	06/2014	2.40	2.93	0.07	2.46	7.21	24	2.41
	07/2014	2.79	2.444	0.107	4.39	7.12	25	2.37
	08/2014	2.64	2.07	0.07	3.38	7.24	24	2.6
	09/2014	2.43	2.36	0.07	2.97	7.45	22	2.08
	10/2014	3.19	3	0.074	2.47	7.28	16	2.55
	11/2014	2.85	2.25	0.08	3.17	7.19	9	2.08
	12/2014	3.61	3.09	0.137	4.43	7.10	8	2.04
	2	02/2014	2.50	2.08	0.11	0.13	7.22	4
03/2014		1.56	1.25	0.054	4.32	8	7.2	1.9
04/2014		1.86	1.6	0.071	4.55	7.35	14	2.2
05/2014		2.99	2.88	0.12	4.03	7.30	23	2.10
06/2014		2.67	2.77	0.07	2.67	7.21	23	2.07
07/2014		2.27	1.96	0.082	4.18	7.26	25	2.19
08/2014		2.03	1.89	0.07	3.70	7.29	24	2.37
09/2014		2.4	2.81	0.07	2.49	7.51	20	2.17
10/2014		3.37	3.03	0.083	2.74	7.29	18	2.09
11/2014		2.93	2.55	0.10	3.73	7.25	7	1.87
12/2014		1.59	1.39	0.121	8.71	7.2	4	1.97
3		02/2014	2.45	1.84	0.11	5.98	7.13	5
	03/2014	1.96	1.56	0.08	5.19	7.09	8	2.1
	04/2014	1.94	1.54	0.082	5.32	7.15	16	2.1
	05/2014	2.38	2.55	0.09	3.33	7.21	22	2.38
	06/2014	2.25	2.08	0.077	3.70	7.04	25	2.6
	07/2014	2.61	2.26	0.10	4.38	7.02	25	2.76
	08/2014	2.09	1.63	0.08	4.91	7.37	26	2.65
	09/2014	1.98	1.70	0.07	4.12	7.45	22	2.59
	10/2014	3.17	2.76	0.081	2.93	7.22	17	2.28
	11/2014	2.52	2.4	0.092	3.83	7.12	10	2.31
	12/2014	2.55	2.25	0.104	4.62	7.15	6	2.2
	4	06/2012	2.80	2.60	n.m	n.m	7.10	26
5	03/2015	6.26	6.43	0.10	1.50	8.50	4.4	1.6
	03/2015	5.98	5.21	0.10	1.91	8.30	7	0.8
6	03/2015	2.72	3.19	0.11	3.46	7.55	6	2.1
7	03/2015	5.24	6.03	0.18	2.92	7.20	12	1.8
8	03/2015	5.81	6.80	0.10	1.48	8.70	10	1.7

n.m – not measured

2.3. Analytical methods

Solid phase extraction (SPE) was used to pre-concentrate DCBQ. The raw water samples were filtered before extraction to minimize undesired loading on the SPE cartridges. For extraction, Waters Oasis HLB cartridges (6 mL, 200 mg adsorbent per cartridge) mounted on a vacuum manifold (Vac Elute SPE 24) was used. The SPE extraction was altered from the previous methods (Zhao et al., 2010). The solvents used for SPE were acidified with 0.25 % formic acid (FA). Prior to sample loading, the SPE cartridges were activated with 6 mL acidified methanol followed by 6 mL acidified water. Each sample was loaded onto the cartridges at a flow rate of approximately 4 mL/min. The cartridges were then washed with 6 mL acidified water followed by 6 mL acidified methanol/water (v/v 50/50) and dried under vacuum for about 5 minutes. The analytes were eluted after soaking the adsorbent with 6 mL acidified methanol for 5-10 min and 0.4 mL acidified water was added to the extracts to prevent loss of analytes. The extracts were then dried down to 0.5 mL (80:20 water: methanol) by nitrogen drying at 13-15 psi in a Zymark TurboVap LV evaporator. For DCBQ analysis, an HPLC separation module (Alliance Waters 2695) was combined with a triple quadrupole tandem mass spectrometer (Quattro Micro API- QAA 624). A Luna C18 (2) column (100X2 mm; 3 μ m, 100 Å) was used with mobile phase consisting 0.25% FA in water (Solvent A) and 0.25% FA in methanol (Solvent B). A 100 μ l volume of the extract was injected with a solvent gradient program of 20 % solvent B at t= 0, linearly increased to 90 % in 20 min and held for 5 min, decreased to 20 % at 25 min and held for 15 min, all at a flow rate of 0.15 mL/min. The mass spectrometer was operated under negative electrospray ionization (ESI) condition with multiple reaction monitoring (MRM). The optimized MS instrumental parameters are presented in Table S2. DCBQ spectra and chromatograms have been presented in Figure S2. DCBQ concentrations were calculated using method calibration curves generated from extraction of standards at a range of concentrations and recoveries were estimated by comparison to standard machine

calibration curves. DCBQ recoveries were consistently over 60 %. The uncertainty as determined by analysis of seven replicate samples of 50 ng/L was 9%. THM analysis was performed according to USEPA Method 551.1 that used liquid/liquid extraction with pentane followed by gas chromatography and electron capture detection (GC/ECD).

2.4. Formation potential tests and persistence experiments

Chlorination and chloramination at 5 mg/L as free and combined chlorine respectively were carried out on each lignin compound at 5 μ M using 300 mL glass stoppered bottles and stored head space free at 25 °C for 6 hours. Figure 2 presents the experimental design for these experiments. The pH of each sample was controlled at 7 using phosphate buffer at 10 mM and the pH varied less than 0.4 units over the reaction period. After 6 h, the free chlorine in each sample was quenched with 0.25 % FA and immediately extracted. Triplicate experiments were carried out for both chlorination and chloramination. For chloramination experiments performed monochloramine was prepared by mixing sodium hypochlorite solution to ammonium chloride solution buffered at pH 8.5 resulting in a 1:1 molar ratio of Cl_2/N . DPD ferrous titrimetric method was used to both standardize solutions and measure chlorine residuals at the end of the test period (APHA et al., 1999). Hypochlorite and monochloramine solutions were freshly prepared and standardized before each experiment. For determining DCBQ persistence, a high concentration (~800 ng/mL) of DCBQ standard in water buffered to different pHs at 10 mM was subjected to continuous injection on the LCMS over 3.3 hours. The buffers used for the different pHs were as follows: phosphate for pH 2.7, citrate for pH 3.5, acetate for 5.5, phosphate for pH 6.7-7.2, borate for 7.8-9 and carbonate for pH 11, all at 10 mM. The pHs varied less than 0.08 units by the end of the reaction period. The time to first injection was controlled to less than 3 min. The concentrations were calculated using calibration from standards in acidified water.

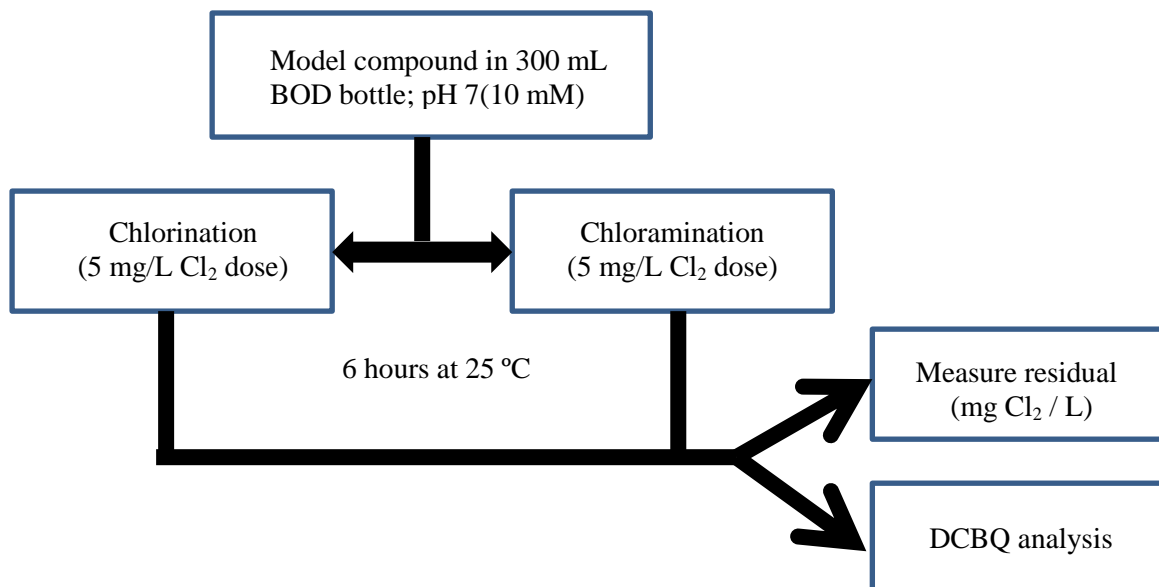


Figure 2: Design of laboratory DCBQ formation potential experiments.

2.5. Quality assurance and control

A travel blank was included in all samplings and shipments. Two SPE blank samples (500 mL Milli-Q water), with and without formic acid were extracted along with other samples in each batch of SPE to examine any contamination during pretreatment. Analysis blank samples (80/20 v/v water/methanol) in a batch run ensured no contamination occurred during analysis. Recoveries were obtained from standards spiked in water: methanol (80/20 v/v). Duplicate extractions or duplicate runs were performed on the samples for occurrence studies. Blanks were included in formation potential experiments to ensure demand-free glassware and buffer solutions. Persistence experiments consisted of analysis blank samples (Milli Q water), both acidified and buffered. DCBQ was not detected in any of the blank samples ensuring no contamination occurred during the experiments. To ensure consistent calibration, DCBQ stability in solvents was investigated (Figure S3) prior to formation and persistence experiments.

3. Results and discussion

3.1 DCBQ occurrence in US utilities

DCBQ occurrence frequency and concentrations in 8 drinking water treatment systems in the USA were investigated. Figure 3 presents a summary of DCBQ concentrations detected in the WTPs along with pH and residual disinfectant concentrations. DCBQ was not detected in any of the source water samples analyzed. The DCBQ level in most POE samples was < 50 ng/L with the exception of WTP 4 which had the highest DCBQ concentration of ~263 ng/L. This was almost ten times higher than in other WTPs and can be primarily attributed to free chlorine being used as secondary disinfectant. Despite WTP 6 and 7 using free chlorine, DCBQ was only 5-17 % of that in WTP 4 and this could be due to difference in water quality characteristics like nature and amount of organic matter, water temperature, water chemistry and mixing conditions at the sampling point.

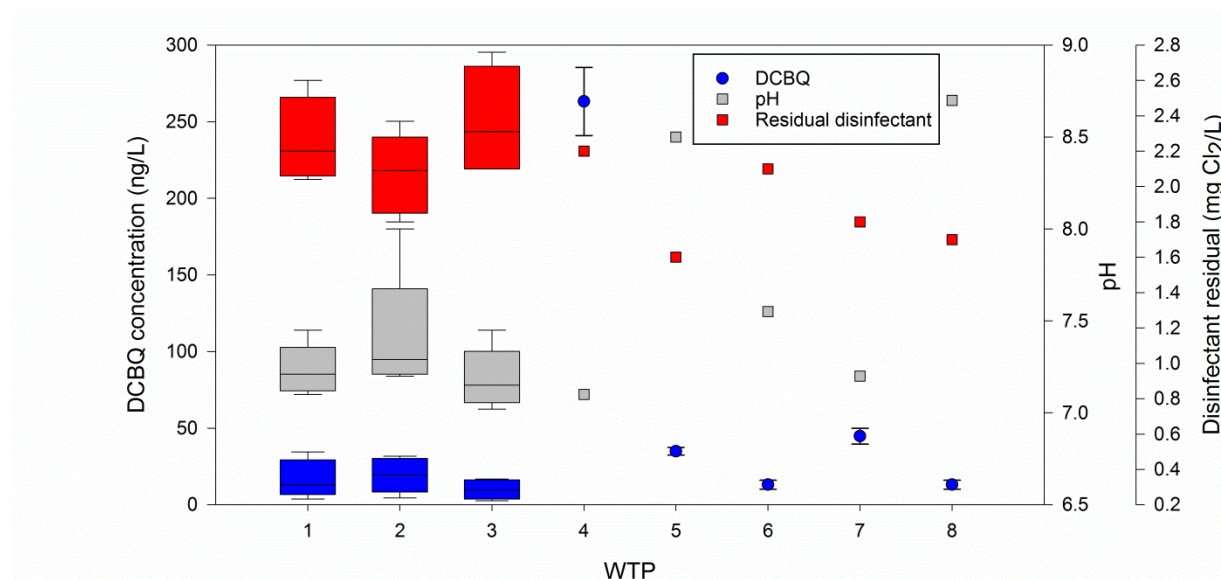


Figure 3: DCBQ concentrations in US utilities.

DCBQ concentrations in each water sample are presented in Table S3. Figure 3 presents DCBQ occurrence frequencies in POE and DS samples. The POE samples had concentrations ranging from 2.6 to 263.2 ng/L and a median of 13 ng/L. 92.3 % of DS-POE samples were from WTPs that used combined chlorine while the remaining were free chlorine samples. 90 %

of the DS-POE samples had DCBQ concentrations < 34.4 ng/L. 66.7 % of the remaining samples that had DCBQ at > 34.4 ng/L were from WTPs that used free chlorine treatment. In contrast, one sample (from WTP 7) that used free chlorine had DCBQ at median concentration which was less than other free chlorine samples. Median and maximum DCBQ concentrations in the distribution systems were 11 ng/L and 162 ng/L respectively. 89.6 % of DS samples were from WTPs using combined chlorine while the remaining 10.4 % used free chlorine. 90 % of the DS samples had DCBQ concentrations < 33 ng/L, 97.2 % of which were combined chlorine samples. From the remaining 10% DS samples that had DCBQ at > 33 ng/L, 85.7 % used free chlorine. It can be inferred that most of the POE and DS samples that had DCBQ concentrations > 90th percentile concentrations were from WTPs that used free chlorine. It is known that the formation of THMs and HAAs from chloramination is much less than from an equivalent dose of free chlorine (McGuire et al., 2002). Evidence to date suggests that the same may be true for DCBQ (Zhao et al., 2012) and this is further reinforced through the results from this study.

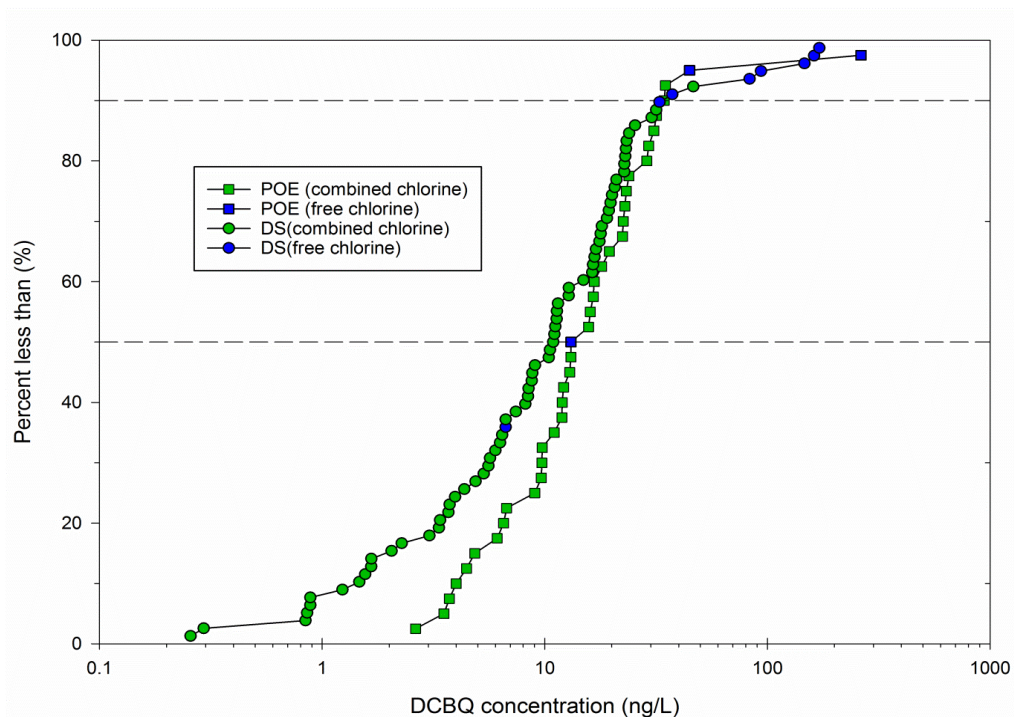
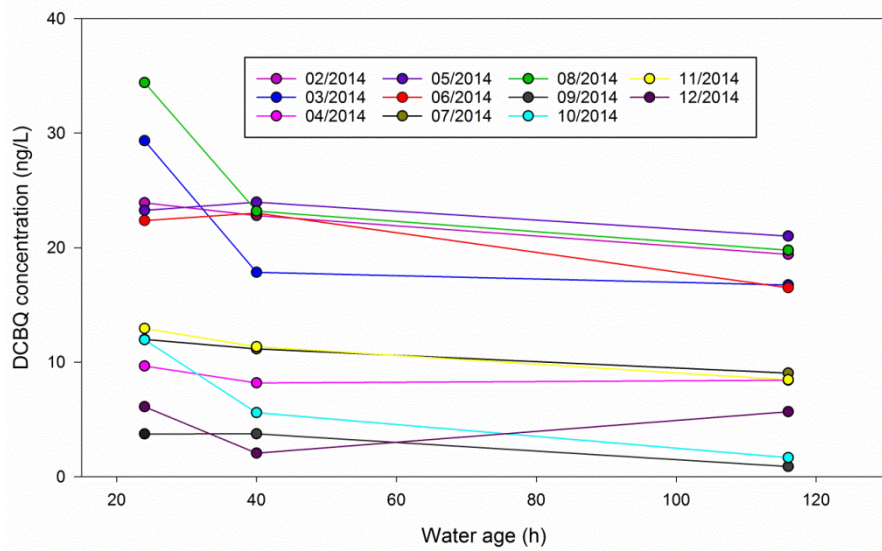
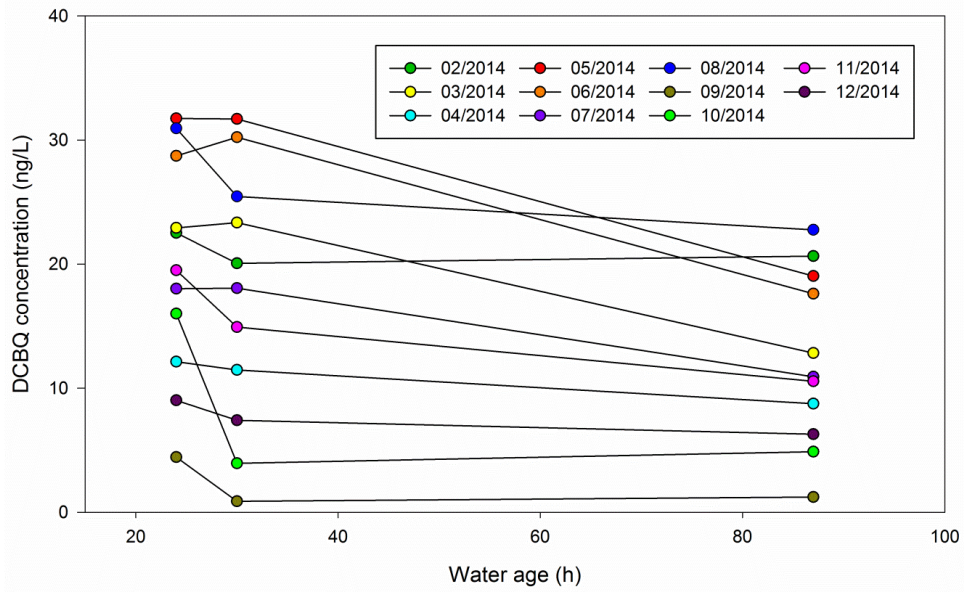


Figure 4: DCBQ occurrence frequencies in US utilities. Median concentrations at POE and DS were 13 and 11 ng/L respectively. 90th percentile concentrations at POE and DS were ~34.4 ng/L and ~33 ng/L respectively.

DCBQ concentrations across distribution systems were assessed for three WTPs. For WTP 1 and 2, a series of sampling events was carried out at the DS-POE and two points in the distribution system consisting of a short and long water age location (Figure 4a and 4b). Relative drop from DS-POE concentrations were 7-86 % and 8.3-72.3 % for WTP 1 and 2 respectively. For WTP 4, one sampling event was carried out at a range of water ages to investigate the fate of DCBQ as compared to the regulated THMs. Percent DCBQ loss from POE was 38.3- 87.5 %. Correlation analysis between water age and DCBQ concentrations for WTP 4 showed a significant negative correlation ($p = 0.008$, $R^2 = 0.72$). Multiple linear regression was used to determine the relationship between water age and DCBQ concentrations: $DCBQ = -0.827[\text{water age}] + 212.89$. For TTHMs, significant positive correlation ($p = 0.008$, $R^2 = 0.712$) existed with water age and the relationship was obtained as $TTHM = 0.155[\text{water age}] + 36.679$. These models are specific to WTP 4 and cannot be used as predictive equations for DCBQ or TTHMs in water considering the possibilities of parallel formation and loss at typical drinking water conditions. However, they could be used to assess potential trends in the fate of DCBQ and TTHM.



**Figure 5: Varying DCBQ concentrations from POE to DS over the sampling period.
(a) WTP 1, (b) WTP 2.**

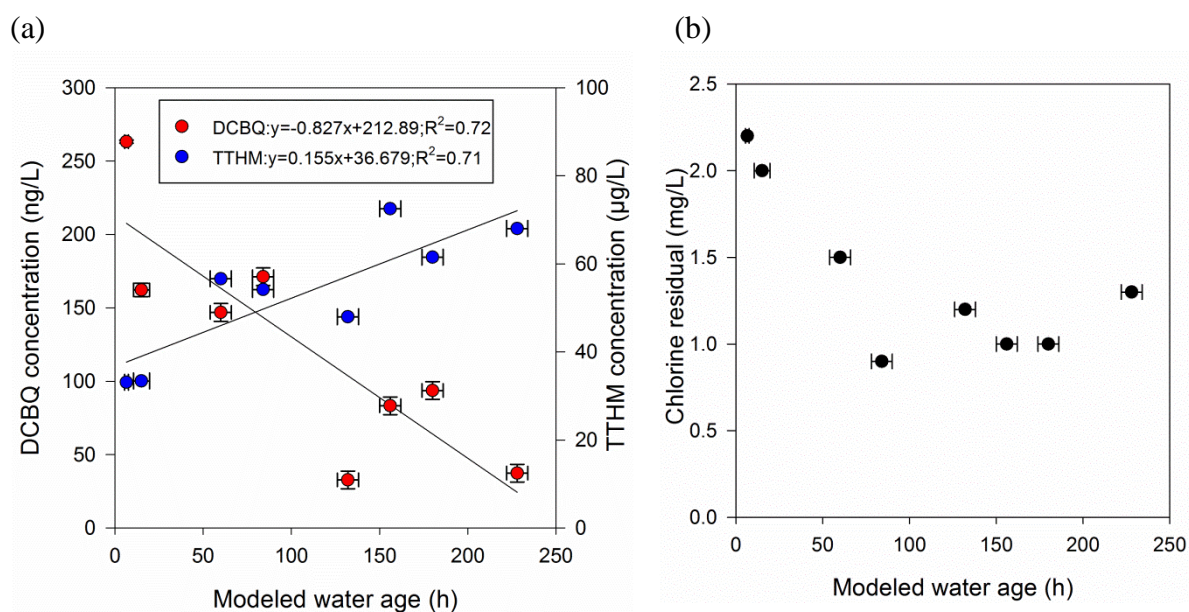


Figure 6: (a) Linear correlations of DCBQ and TTHM concentrations with water ages for WTP 4; (b) Residual chlorine across water ages. Vertical error bars are standard deviations of duplicate experiments. Horizontal error bars are standard deviations of the modeled water ages.

3.2. DCBQ yields of lignin monomers during chlorination and chloramination

Figure 6 presents the DCBQ yields from chlorination of lignin monomers calculated as molar yield in percentage as well as the molar free chlorine demands. DCBQ yields from chlorination of lignin groups varied from 0% (alkoxy group, catechol, ferulic acid) to 0.8 % (p-hydroxy benzaldehyde). Other groups showed little or no DCBQ yield. For chloramination, DCBQ was not detected. This is in agreement with results from a prior study where yields of products from chlorination of phenol were at least 10 times higher than from chloramination (Zhao et al., 2012). However, for typical scenarios in drinking water treatment, DCBQ yields may be influenced by water age, alkaline pH conditions, disinfectant residuals, temperature and actual NOM composition. This is the first study that specifically examined DCBQ yields from lignin groups and hence a comparison could not be made. While the disinfection conditions used in this study ($\text{Cl}_2 = 5 \text{ mg/L}$, $\text{NH}_2\text{Cl} = 5 \text{ mg/L}$ as Cl_2 , pH 7, reaction time = 6 h) were selected to mimic the conditions that are typical of water treatment systems, longer reaction

times (> 6 h) and residuals in excess of 0.6 mg/L Cl₂ were avoided to minimize the possibility of simultaneous DCBQ degradation.

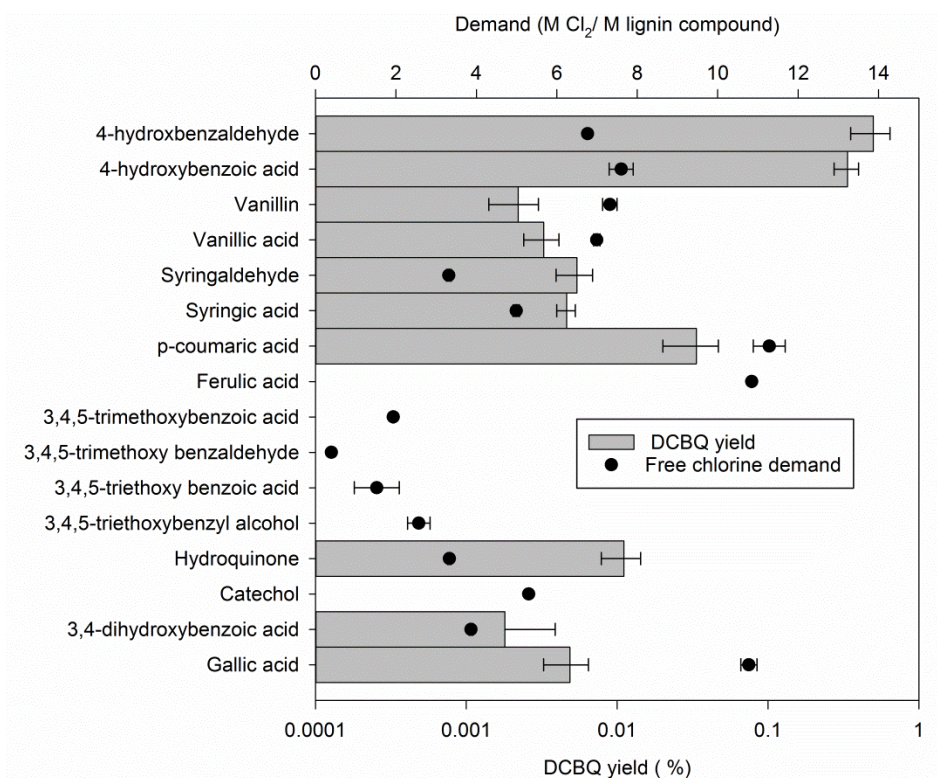


Figure 7: DCBQ yields from chlorination of lignin compounds. Error bars represent standard deviations of triplicate experiments. Symbols represent free chlorine demand. Corresponding error bars are standard deviations from duplicate measurements.

Among the lignin classes considered, the yield from chlorination of p-hydroxyl phenols was the highest (0.6-0.8%), which is at least 100 times more than the other lignin monomers. It appears that the electron donating -OH group in p-hydroxybenzoic acid activated the ring towards electrophilic aromatic substitution in the vacant ortho sites and oxidative decarboxylation forming 2, 4, 6-trichlorophenol (Larson and Rockwell, 1979) and other chlorophenolic intermediates which could all be potential DCBQ precursors. Figure 7 presents DCBQ formation through a mechanism that involves successive attack on 2, 4, 6-trichlorophenol (1) by nucleophile OH⁻ (or OCl⁻) at ortho position to phenolic group. The more reduced form p-hydroxybenzaldehyde, is also expected to react similarly, perhaps through initial oxidation. The proposed mechanism might also apply to p-coumaric acid that produced

at least 10 times more DCBQ yield than the rest. However, its methoxy derivative ferulic acid was not an active DCBQ precursor. Similar differences have been noted in their yields of known DBPs: while p-coumaric acid produced 14 % yield of DCAA and 68 % unknown TOX, neither was produced from ferulic acid (Bull et al., 2006).

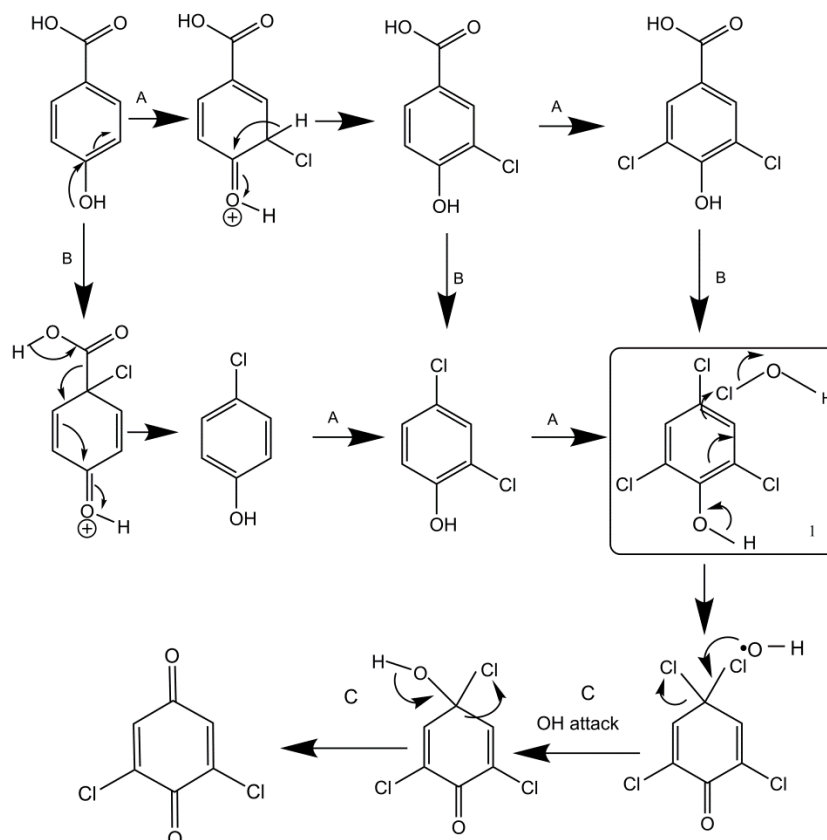


Figure 8: Proposed mechanism for formation of 2,6-DCBQ from chlorination of p-hydroxybenzoic acid (extension to Larson and Rockwell, 1979); A-electrophilic aromatic substitution, B-oxidative decarboxylation, C- nucleophilic attack.

For vanillin and syringyl phenols (methoxy derivatives of p-hydroxyl phenols), the most likely reason for relatively trivial DCBQ yields (0.004-0.009%) could be that the positions ortho to the OH are occupied by groups that cannot participate in the proposed mechanism ($-\text{OCH}_3$). Despite the noted resemblance in reactivity and yields of vanillic acid and p-hydroxybenzoic acid, chlorination of the former could result in unsaturated methoxy acids with little or no chlorophenol formation (Bull et al., 2006). However, Larson and Rockwell (1979) reported decarboxylation of vanillic acid with slower kinetics than p-

hydroxybenzoic acid, forming chlorophenols like 4-chloro-2-methoxyphenol and dichloro-2-methoxyphenol. This explanation also applies to vanillin which is a derivative of vanillic acid. For syringyl groups chlorination could result in methoxy chlorophenols with ultimate reactions analogous to p-hydroxybenzoic acid involving oxidation followed by fragmentation and cleavage of the structure (Bull et al., 2006). Therefore, slower kinetics of reaction with chlorine due to partially-filled (vanillin phenols) or completely filled (syringyl phenols) ortho sites may inhibit chlorine substitution and DCBQ formation.

The DCBQ formed from hydroquinone was 0.02 % while catechol was not an active precursor. Bull et al., (2006) proposed a pathway for these phenols that involves quinone formation followed by HOCl addition across double bonds. Therefore, for hydroquinones there is potential for formation of 1, 4-benzoquinones which can result in some DCBQ formation. For a similar reaction with catechol, chlorinated 1, 2-benzoquinones may be formed which could produce largely oxygenated aliphatic compounds resulting in no DCBQ formation. Gallic acid produced a relatively low DCBQ yield of 0.008 % while 3,4-dihydroxybenzoic acid did not produce DCBQ probably due to the absence of chloro-phenolic intermediates (Larson and Rockwell, 1979) .

The tri-alkoxy groups consumed relatively less chlorine (0.4-2.6 M Cl₂/M compound) which is justified considering the ether groups are highly deactivating. This low reactivity could mean no significant modification of the ring through substitution, oxidation or fragmentation which is essential for DCBQ formation. Most of the attack by chlorine may be concentrated at the sites away from the ring and not on the ring itself and this can suppress DCBQ formation. It can be inferred from these results that, although activating –OH unit contributes significantly to DCBQ formation, excessive activation and addition of methoxy groups can obstruct DCBQ formation.

The reactivity based on chlorine demand follows the order cinnamyl phenols > p-hydroxyl phenols and vanillin phenols > syringyl phenols and polyphenols > alkoxy groups. However, the chlorine demand for gallic acid (a polyphenol) was as high as the cinnamyl group, while the corresponding combined chlorine demands were almost halved. The combined chlorine demand for the lignin phenols ranged from 1.85-5.2 M Cl₂/M compound. Relatively low DCBQ formation from phenols with high chlorine demand suggests that most of the chlorine might have resulted in oxidation rather than substitution. In general, both chlorination and chloramination of lignin phenols are expected to produce products chlorinated at the ortho and para positions although chloramination would have slower reaction kinetics which is likely why no DCBQ was observed in the 6 h reaction period.

3.3 DCBQ persistence

A series of controlled laboratory experiments (20 °C) were conducted on DCBQ solutions at varying pHs in the absence of disinfectant residuals to avoid the complication of parallel reactions of DCBQ with disinfectants. These solutions were analyzed periodically for residual DCBQ. Treated drinking water is generally distributed at a pH range 7.5-9.6. However, acidic pHs and a very high pH of 11 were also used to examine DCBQ stability at extreme pH conditions (Figure S5). These tests showed that DCBQ was stable in water at acidic pH conditions (pH 2.7-6.7). At pH 11 no DCBQ was detected even for the first injection (t=0). At pH 9, DCBQ concentrations decreased by 98 % in 80 min and fell below detection limit in the subsequent injections. Only DCBQ degradation profiles at pHs relevant to drinking water treatment (7.2, 7.8 and 8.2) have been presented. Natural-log plots of DCBQ concentration versus time at these pHs are presented in Figure 7a. Linear response indicated a rate law that is first order in DCBQ. Also observed was an increasing rate of DCBQ loss with increasing pH. At the end of the testing period, the initial concentrations at pHs 7.2, 7.8 and 8.2 decreased by

29%, 73% and 94% respectively. The observed first order rate constants plotted against molar OH⁻ concentrations are presented in Figure 7b. Linear regression resulted in a line of slope 0.997 with a very small intercept which indicated that the hydrolysis can be treated as first order in hydroxide. Based on the data presented, the following pseudo-first order rate law can be proposed, to simulate typical variations for drinking water:

$$r = \frac{-d[DCBQ]}{dt} = k_{obs} [DCBQ] \quad (M s^{-1}) \quad (1)$$

$$k_{obs} = k_{actual}[OH^{-}] \quad (2)$$

$$k_{actual} = k_2 = 156 M^{-1}s^{-1}$$

where,

k_{obs} is the observed or pseudo first order rate constant (s^{-1})

k_2 is the actual or second order rate constant ($M^{-1} s^{-1}$)

The value of rate constants were estimated by minimizing the sum of the squares of the weighted deviations between measured and predicted residual values. The initial DCBQ concentrations for the model were estimated from intercepts of observed data. Figure 8 shows the measured and predicted DCBQ degradation at pHs 7.2, 7.8 and 8.2. The model was a good indicator of the pH-dependent DCBQ degradation ($R^2 > 0.9$, $p < 0.0001$) (Figure S6). The stability decreased with increasing pH with rate constants at pHs 7.2, 7.8 and 8.2 being 0.28×10^{-4} , 1.1×10^{-4} and $2.4 \times 10^{-4} s^{-1}$ respectively. The half-life of DCBQ at pH 7.2 was 7.6 h which was close to Qin's observation that half-life of DCBQ at pH 7 was 6-7 h (Zhao et al., 2012). At pHs 7.8 and 8.2, half-lives were approximately 2 h and 0.8 h respectively. The modeled half-lives at pHs 9 and 11 were 7.8 min and 4.8 s respectively which explain the rapid degradation observed in the experiment. Studies reported in literature lack quantitative kinetic analysis on DCBQ degradation, so a comparison could not be made.

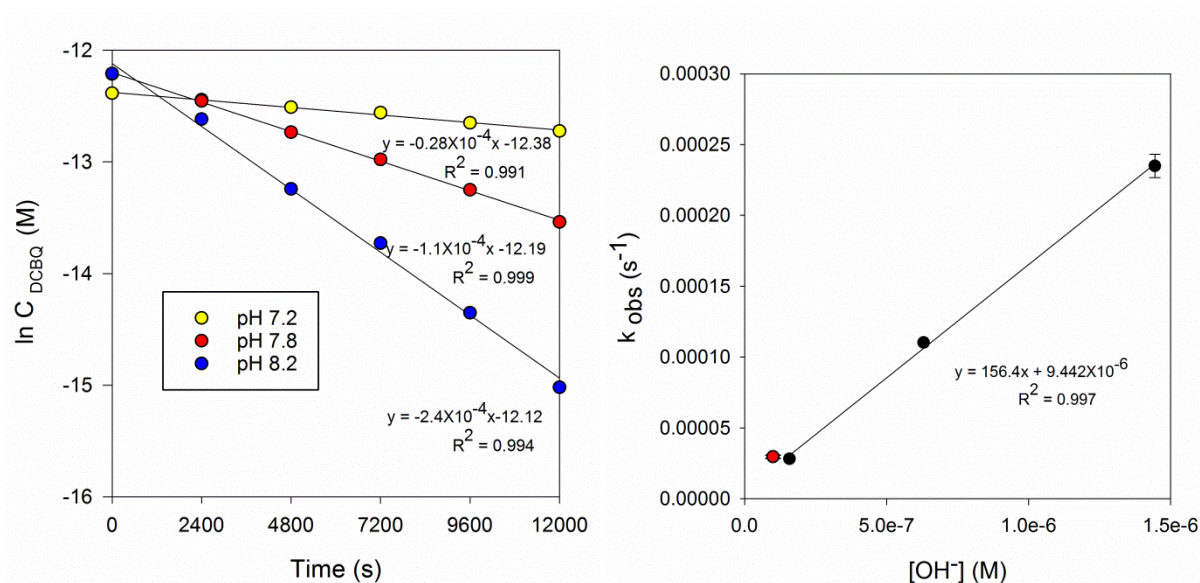


Figure 9: Kinetic analysis of DCBQ degradation in the absence of free chlorine (20 °C). (a) Natural-log plot of DCBQ concentrations vs time; (b) Relationship between pH and first order rate constants of DCBQ. Data point in red was estimated from half-life reported in Qin et al., 2011.

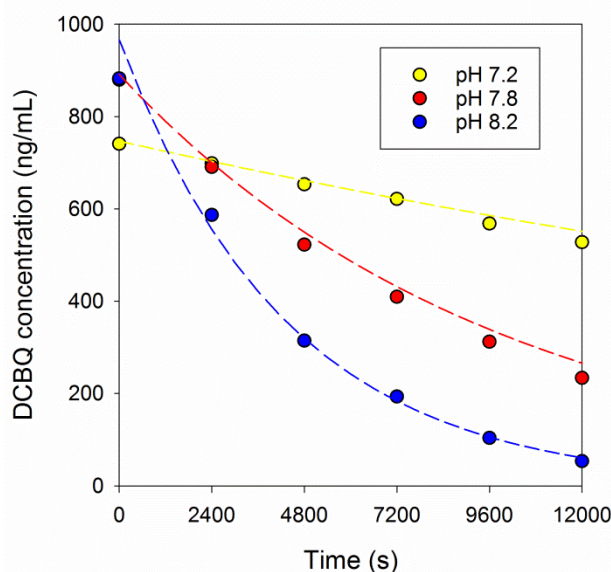


Figure 10: DCBQ degradation at different pHs. The symbols represent the measured data and the lines represent the modeled DCBQ degradation. Experimental conditions: T = 20 °C; 10 mM buffer; ~800 ng/mL DCBQ.

4. Implications on drinking water treatment

Health concerns relating to emerging carcinogenic DBPs provide a compelling motivation for addressing the occurrence and formation of halobenzoquinones (HBQ) in treated drinking waters. Most DBP control strategies focus on the formation of regulated DBPs. Regulations for

emerging DBPs like DCBQ need attention. Differences in the DCBQ formation may be attributed to fundamental differences in characteristics of precursor material in source waters. Results from this study reinforce the hypothesis that lignin phenols might be DCBQ precursors, although significant DCBQ formation was observed only from chlorination of p-hydroxyl phenols. However, this indicated that DCBQ formation would be enhanced by activated aromatic centers in NOM that contain hydroxyl groups with vacant ortho positions. DCBQ formation during chloramination was not as significant for the reaction period considered (6 h) which could be due to the chemistry and slower kinetics of chloramination reactions. Despite this, chloraminated drinking waters from occurrence studies had DCBQ at detectable concentrations. It is probable that the water ages of the samples being at least ten times greater than the reaction period used in formation potential tests allowed a longer reaction time, although simultaneous degradation is also expected at these pHs. These results have implications for addressing DCBQ formation and fate in natural waters and its exposure in distribution systems. The results of this study indicate that $[\text{OH}^-]$ catalyzes DCBQ degradation as indicated by the increasing first-order rate constant (k_{obs}) with increasing pHs. Figure 9 represents the t_{50} and t_{10} values for DCBQ at drinking water pHs, which indicate the time to 50 % and 90 % DCBQ degradation respectively. At these pHs, DCBQ half-life shortens, which in addition to the effect of disinfectant residuals would play an important role in exposure studies since the total DCBQ formed may be substantially greater from what is measured in treated waters. This also justifies the sampling protocol requirements for water pH adjustment in the field to ensure accurate results.

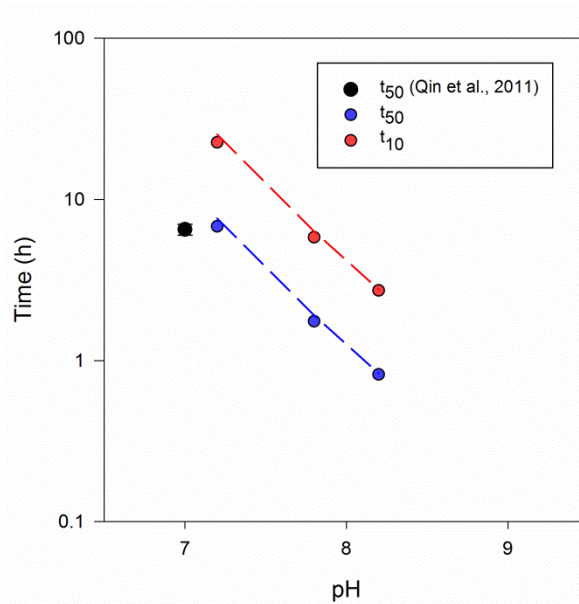


Figure 11: Observed and modeled t_{10} and t_{50} values for DCBQ plotted against pH. The symbols represent measured data and the lines represent modeled DCBQ degradation.

4.1 Recommendations

Future research needs to include DCBQ formation from other disinfection treatments like ozonation plus chlorination, ozonation plus chloramination, chlorine dioxide, UV irradiation, UV plus ozone, etc. on lignin monomers. DCBQ formed from these precursors in relation to total organic halide (TOX) needs research attention. Also, there is clear need for better understanding of DCBQ stability in distribution systems in the presence of disinfectant residuals. Developing an integrated model that includes the effect of both pH and disinfectant residual could help better estimate DCBQ exposure.

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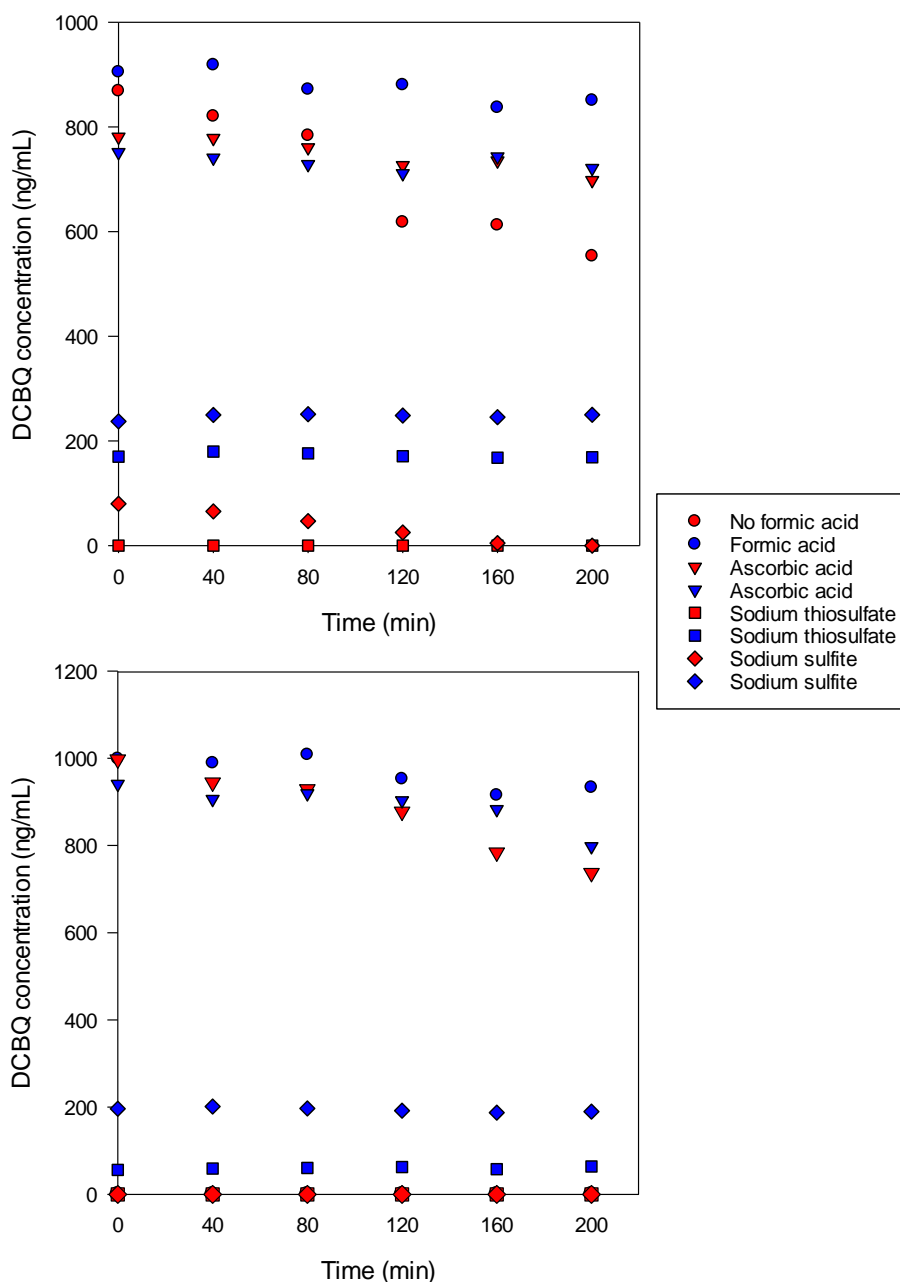
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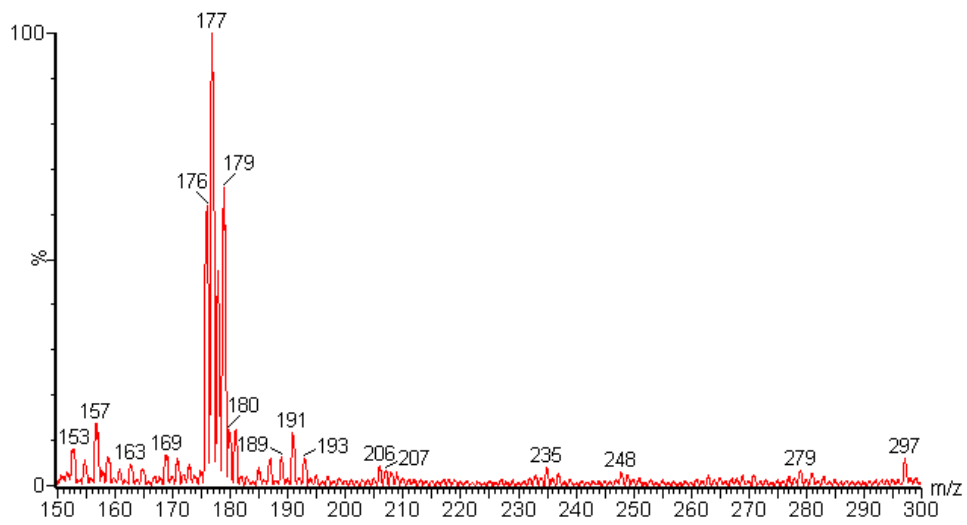
Figure S1: Evaluating different preservatives for DCBQ in the presence of:
a) Combined chlorine, (b) free chlorine.



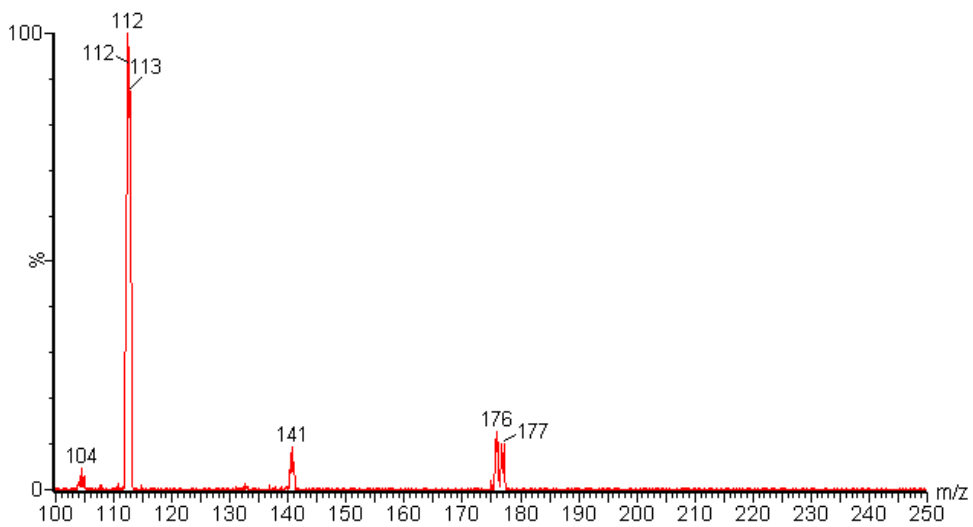
2, 6-DCBQ at 1000ng/mL was spiked in samples containing 70 μ M (5mg/L) of disinfectant with and without preserving agents (500 μ M). Ascorbic acid, sodium sulfite and sodium thiosulfate were used with and without formic acid (lowers pH to ~2) considering DCBQ stability is also affected by pH. With sodium thiosulfate and sodium sulfite ~75% of DCBQ appeared to be lost probably due to reactions with DCBQ. DCBQ was stable in the solutions containing ascorbic acid with and without formic acid. Formic acid by itself preserved DCBQ in the presence of both free chlorine and combined chlorine. Therefore, formic acid was chosen as sample preservative.

Figure S2: DCBQ mass spectra and chromatogram.

(a) Mass spectrum of DCBQ parent mass (m/z 177)



(b) Mass spectrum of DCBQ daughter (m/z 112)



(c) DCBQ chromatogram (Retention time ~ 15min)

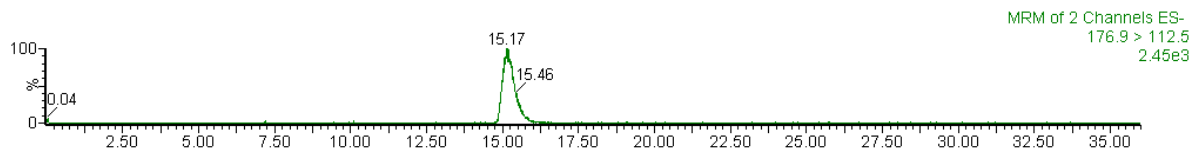
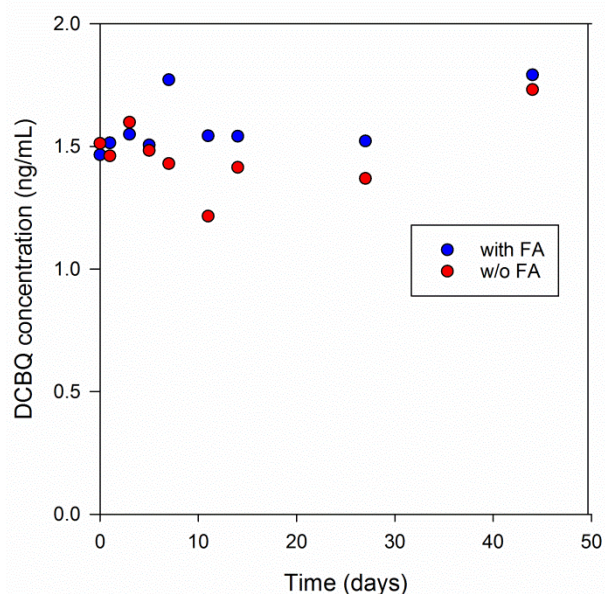
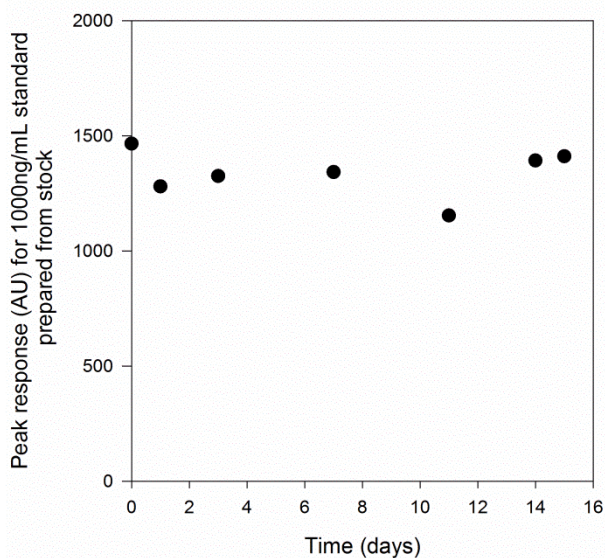


Figure S3: DCBQ stability in solvents



To identify stability issues with DCBQ stock solutions in methanol and standards in a mixture of water and methanol (v/v 80:20), working solutions were subjected to analysis over 15 days. Stock solution (1 mg/mL) was prepared in LCMS grade methanol using volumetric flasks and stored at 20 °C. A standard of 1000 ng/mL was prepared from this stock and analyzed on a timely basis to observe DCBQ stability in methanol. Also, two sets of calibration standards made of water/methanol (v/v 80:20), with one set acidified with 0.25 % FA were stored at 20 °C and analyzed over the 15 day period to observe any degradation in the form of change in slope of calibration curve. DCBQ was stable in either case over the test period.

Figure S4: Effect of chlorine residual on DCBQ

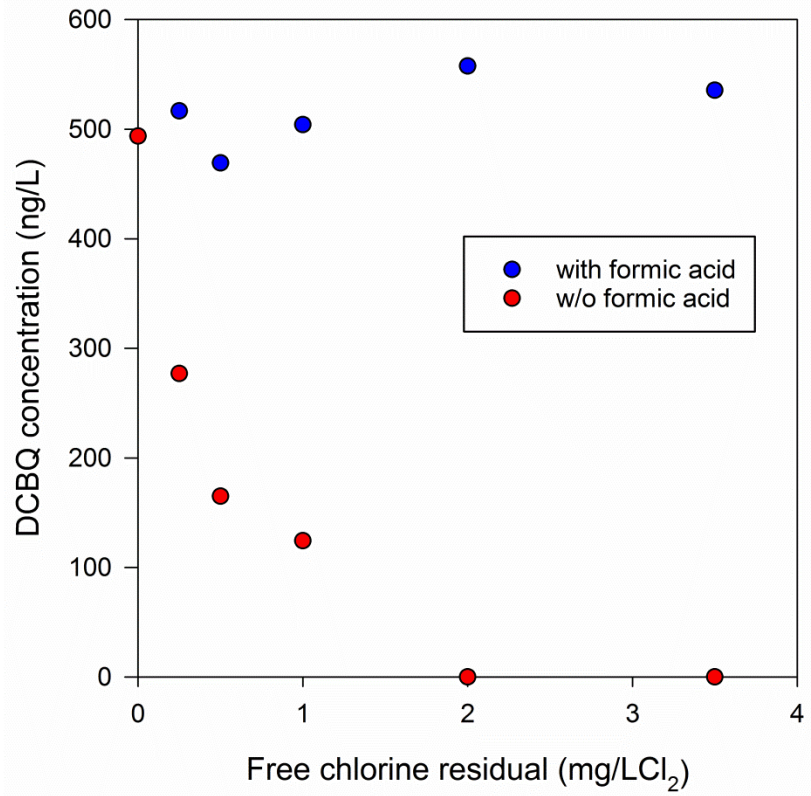


Figure S5: DCBQ stability at extreme pH conditions.

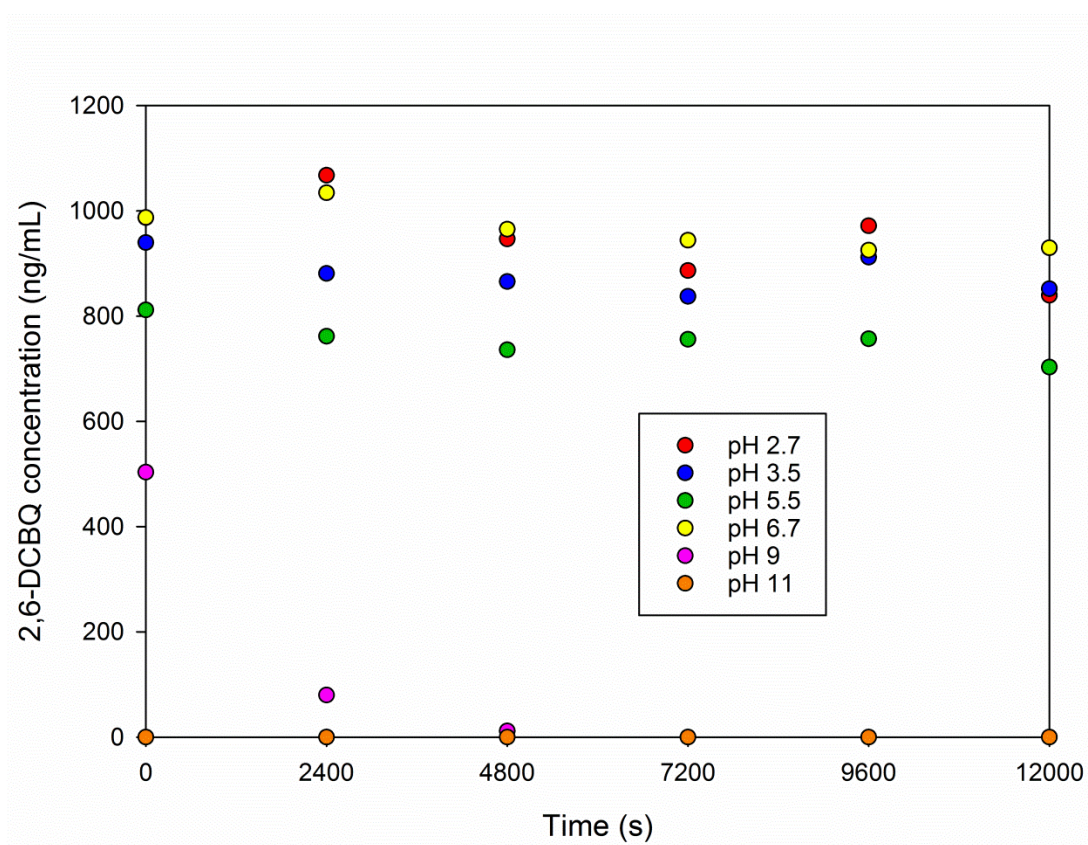


Figure S6: Observed vs predicted DCBQ concentrations at different pHs.

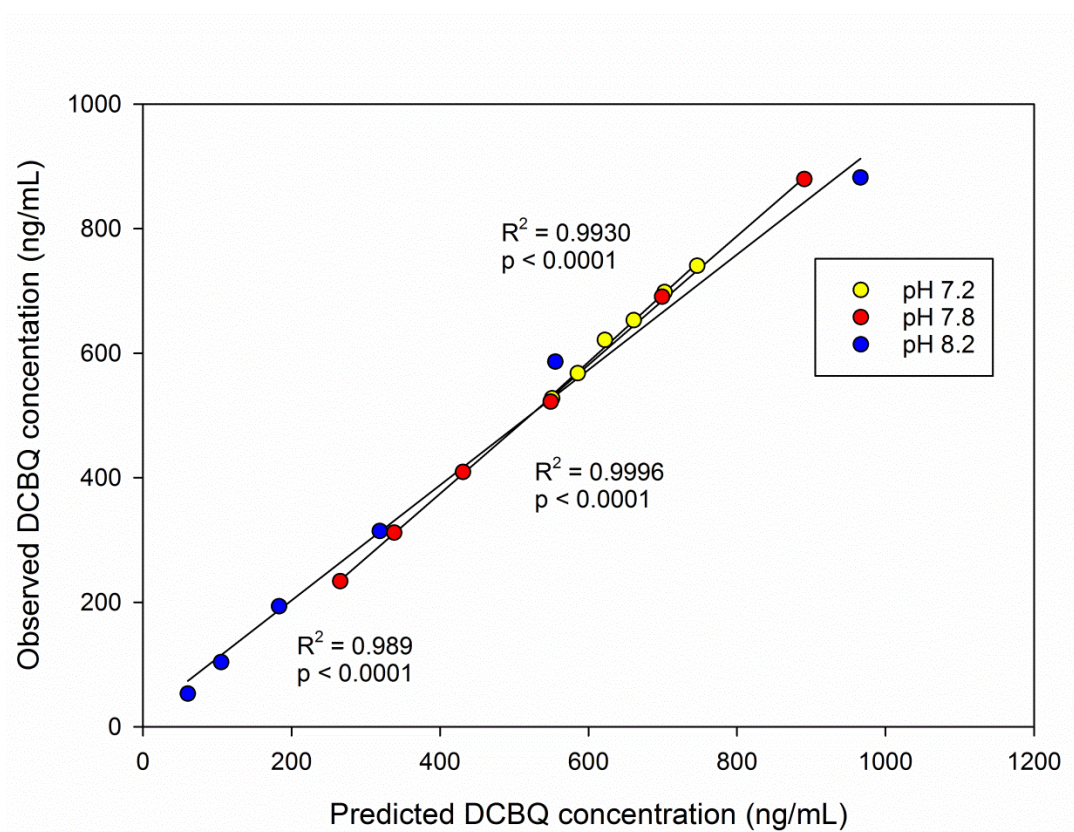


Table S1.a: Summary of treatment process in water treatment plants (WTPs).

WTP	1	2	3	4	5	6	7	8
Activated carbon					X	X		
Coagulation	X	X	X	X	X	X	X	X
Sedimentation	X	X	X	X		X		X
Filtration	X	X	X	X	X	X	X	X

WTP 1-4 –river water source; WTP 5, 6, 8 – reservoir source; WTP 7-ground water source
WTP 1 and 2 shared the same raw water.

Table S1.b: Disinfectants used in WTPs.

WTP	Primary disinfectant	Secondary Disinfectant
1	Free chlorine	Chloramine
2	Free chlorine	Chloramine
3	Free chlorine	Chloramine
4	Chlorine dioxide	Free chlorine
5	Free chlorine	Chloramine
6	Free chlorine	Free chlorine
7	Free chlorine	Free chlorine
8	Free chlorine	Chloramine

Table S2: Optimized parameters for DCBQ detection and analysis.

Analyte	Mass transition	Optimized instrument parameters	
		Parameters	Values
DCBQ	176.9>112.8	Collision energy (V)	15
		Capillary (kV)	3.4
		Cone (V)	25
		Source temperature °C	120
		Desolvation temperature °C	300
		Desolvation gas flow (L/h)	325
		Cone gas flow(L/h)	50

Table S3: DCBQ concentrations in samples.

Treatment Plant	Sampling Date	Point of entry (POE)	Distribution System		
		2,6-DCBQ (ng/L)	Water age (h)	2,6-DCBQ (ng/L)	
WTP 1	02/2014	23.9±3.3	40	22.8±2.7	
			116	19.4±2.3	
	03/2014	29.3±2.2	40	17.8±1.01	
			116	16.8±1.9	
	04/2014	9.7±6.4	40	8.2±1.6	
			116	8.4±1.08	
	05/2014	23.2±3.9	40	24±1.9	
			116	21±5.3	
	06/2014	22.4±4.5	40	23±8.3	
			116	16.5±4.7	
	07/2014	12±0.8	40	11.2±0.9	
			116	9.05±2.06	
	08/2014	34.4±1.4	40	23.2±6	
			116	19.78±7.5	
	09/2014	3.7±0.1	40	3.7±0.1	
			116	0.8±0.1	
	10/2014	12±1.3	40	5.6±0.09	
			116	1.6±0.07	
	11/2014	13±0.9	40	11.3±1.6	
			116	8.5±0.09	
	12/2014	6.1±0.5	40	2.04±0.18	
			116	5.7±1.02	
	WTP2	02/2014	22.5±5.8	30	20.06±0.02
				87	20.65±0.7
03/2014		22.9±6.9	30	23.3±0.5	
			87	12.8±3.8	
04/2014		12.1±2.5	30	11.5±2.9	
			87	8.7±0.9	
05/2014		31.7±9.8	30	31.70±1.6	
			87	19.03±6.8	
06/2014		28.72±1.45	30	30.2±0.4	
			87	17.6±5.5	
07/2014		18±4.6	30	18±1.06	
	87		10.9±3.4		
08/2014	30.9±5.5	30	25.5±3.4		
		87	22.8±0.4		
09/2014	4.4±0.1	30	0.9±0.1		
		87	1.2±0.08		
10/2014	16±5.4	30	4±0		
		87	5±0		
11/2014	19.51±3.7	30	14.9±3.2		

			87	10.6±2.9
	12/2014	9±0.1	30	7.4±0.3
			87	6.3±0.3
WTP3	02/2014	16.5±2.2	52	17±1.4
			57	12.8±1.7
	03/2014	9.7±0.9	52	6±0.5
			57	6.4±2
	04/2014	6.5±0.6	52	3.7±0.8
			57	0.8±0.3
	05/2014	16.7±1.6	52	10.4±2.4
			57	3.3±0.2
	06/2014	11±4.6	52	11.3±0.05
			57	11.05±6.7
	07/2014	15.7±2.4	52	16.4±1.3
			57	8.8±0.6
	08/2014	6.7±0.4	52	0.9±0.1
			57	0.3±0.02
	09/2014	2.6±0.49	52	3±0.09
			57	1.6±0.2
	10/2014	4±0	52	1.7±0.3
			57	1.5±0.2
	11/2014	4.8±0.2	52	4.3±0.2
			57	3.4±0.2
	12/2014	9.8±0.3	52	5.3±0.7
			57	2.3±0.3
WTP4	06/2012	263.2±22.15	15	162.2±14.5
			60	146.9±13.3
			84	171.2±15.1
			132	32.8±4.6
			156	83.3±8.4
			180	93.7±9.2
			228	37.4±4.9
WTP5	03/2015	34.9±2.5	-	46.5±5.2
	03/2015	3.5±0.09	-	0.3±0.2
WTP6	03/2015	13.1±2.8	-	6.7±0.7
WTP7	03/2015	44.74±5.2	-	n.s
WTP8	03/2015	13.1±2.9	-	6.7±0.7
Range (ng/L)		2.6-263.2		0.3-162
Median (ng/L)		13		11
n.s-not sampled; - unknown.				