

Evaluation of DBPs formation from SMPs exposed to chlorine, chloramine and ozone

Beibei Zhang, Qiming Xian, Jian Lu, Tingting Gong, Aimin Li and Jianfang Feng

ABSTRACT

Soluble microbial products (SMPs) are an important group of components in wastewater effluents. In this study, the formation of disinfection by-products (DBPs), including trihalomethanes (THMs), haloacetic acids (HAAs), chlorinated solvents (CSs), halo ketones (HKs), haloacetonitriles (HANs) and trichloronitromethane (TCNM) (chloropicrin), from SMPs during chlorination, chloramination and ozonation was investigated. More carbonaceous DBPs (C-DBPs: THMs, HAAs, CSs and HKs) and nitrogenous DBPs (N-DBPs: HANs and TCNM) were formed in chlorination than chloramination. More dichloroacetic and N-DBPs, and higher DBP formation potential were generated by SMPs than by natural organic matter. The results also show that disinfection factors, including temperature, pH, disinfectant dose, reaction time and bromide level significantly affected the formation of DBPs from SMPs. Additionally, the bromine incorporation factor indicates that chloramination may be a good alternative to chlorination in reducing the formation of Br-DBPs from SMPs. Bromide level and pH were the key factors affecting the formation of DBPs in both chlorination and chloramination.

Key words | bromine incorporation factor (BIF), disinfection by-products (DBPs), disinfection methods, influence factors, key factor, soluble microbial products (SMPs)

Beibei Zhang
Qiming Xian (corresponding author)
Tingting Gong
Aimin Li
Jianfang Feng
 State Key Laboratory of Pollution Control and Resource Reuse,
 School of the Environment, Nanjing University,
 Nanjing 210023,
 China
 E-mail: xianqm@nju.edu.cn

Jian Lu
 Key Laboratory of Coastal Environmental Processes and Ecological Remediation,
 Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences,
 Yantai 264003,
 China

ABBREVIATIONS

TCM	Trichloromethane	DBE	1,2-Dibromoethane
BDCM	Bromodichloromethane	PCE	Tetrachloroethylene
DBCM	Dibromochloromethane	DBC	1,2-Dibromo-3-chloropropane
TBM	Tribromomethane	1,1-DCP	1,1-Dichloro-2-propanone
MCAA	Monochloroacetic acid	1,1,1-TCP	1,1,1-Trichloro-2-propanone
MBAA	Monobromoacetic acid	DCAN	Dichloroacetonitrile
BCAA	Bromochloroacetic acid	TCAN	Trichloroacetonitrile
BDCAA	Bromodichloroacetic acid	BCAN	Bromochloroacetonitrile
CDBAA	Chlorodibromoacetic acid	DBAN	Dibromoacetonitrile
DBAA	Dibromoacetic acid		
DCAA	Dichloroacetic acid		
TBAA	Tribromoacetic acid		
TCAA	Trichloroacetic acid		
1,1,1-TCE	1,1,1-Trichloroethane		
CTC	Carbon tetrachloride		

INTRODUCTION

Due to the worldwide shortage of freshwater resources, wastewater reuse has become a promising way to conserve

the limited freshwater resources. To inactivate the pathogenic microorganisms, disinfection must be conducted for wastewater effluents before their reuse. Chlorine has been widely used for disinfection in water treatment owing to its low cost and high efficiency. However, chlorine can also react with organic matter and some inorganic ions to form disinfection by-products (DBPs), such as trihalomethanes (THMs), haloacetic acids (HAAs), halonitromethanes (HNMs), etc. (Hu *et al.* 2010). For the effluents of biological wastewater treatment plants, soluble microbial products (SMPs), which consist of macromolecules and cellular debris including proteins, polysaccharides, humic acids, and DNA, are usually the major components of soluble organic matter (Ni *et al.* 2010). According to previous studies, SMPs were the organic precursors of some DBPs, such as THMs, HAAs and dichloroacetonitrile (DCAN), and could increase the DBPs formation in both wastewater effluent and surface water supply after chlorination (Liu *et al.* 2014).

Previous studies have shown that DBPs were associated with the teratogenic, carcinogenic and mutagenic risks (Plewa *et al.* 2008). In order to lower the ecotoxicity of reuse water, there has been increasing interest in using chloramine or ozone as the alternative disinfectant. However, new problems may occur with these alternative disinfectants. For example, the use of chloramine may lead to a decrease in regulated DBPs, but more nitrogenous DBPs (N-DBPs), such as HNMs and nitrosamines, may be formed (Luo *et al.* 2012; Yang *et al.* 2012). Ozone can significantly reduce or eliminate the formation of THMs and HAAs, however, it can result in the formation of bromate and nitrosamines (von Gunten *et al.* 2010).

The concentrations and speciation of DBPs were significantly affected by water quality parameters and operating conditions. During chlorination/chloramination, the disinfectant dose, natural organic matter (NOM) level and reaction time had positive influence on the formation of THMs and HAAs (Hua & Reckhow 2012; Roccaro *et al.* 2014; Hong *et al.* 2015). High bromide concentration can enhance the formation of bromine-containing DBPs (Br-DBPs) (Chang *et al.* 2001; Hong *et al.* 2013). Increasing pH increased THMs and HNMs yields in chlorination, but decreased THMs and HAAs formation in chloramination (Doederer *et al.* 2014). For ozonation, bromide ions can

promote the formation of Br-DBPs and nitrosamines (von Gunten *et al.* 2010). An increase in the formation of bromate was observed with increasing ozone doses (Zimmermann *et al.* 2011). However, in most of these previous studies, drinking water and wastewater effluent disinfection were studied, and thus NOM was the organic precursor which generated the studied DBPs. Up to now, few studies have been carried out to investigate the formation of DBPs formed by SMPs during disinfection (Liu *et al.* 2014), especially by chloramination and ozonation. Studies regarding the influence factors on the formation of DBPs in chlorination and chloramination of SMPs are even fewer. Since wastewater reuse has become a growing portion of water supplies, and chloramine and ozone have gained more and more popularity in water disinfection, it is quite necessary to compare the formation of DBPs from SMPs under chlorination, chloramination and ozonation with various conditions, and thus provide more information for the disinfection of reuse water.

In this study, the DBPs produced from SMPs under chlorination, chloramination and ozonation were studied and compared. The effects of several factors, including temperature, pH, disinfectant dosage, reaction time and bromide level, on the formation of carbonaceous DBPs (C-DBPs; including four THMs, nine HAAs, five chlorinated solvents (CSs) and two halo ketones (HKs)) and N-DBPs (including four haloacetonitriles (HANs) and trichloronitromethane (TCNM)) were investigated. The bromine incorporation factor (BIF) and the main factors affecting the formation of DBPs from SMPs were also evaluated.

MATERIAL AND METHODS

Chemicals and reagents

Sodium hypochlorite solution (NaClO, 5%) was obtained from Sigma. Standard solutions of THMs (trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM)), CSs (1,1,1-trichloroethane (1,1,1-TCE), carbon tetrachloride (CTC), 1,2-dibromoethane (DBE), tetrachloroethylene (PCE), 1,2-dibromo-3-chloropropane (DBC)), HKs (1,1-dichloro-2-propanone (1,1-DCP); 1,1,1-trichloro-2-propanone (1,1,1-TCP)),

HANs (DCAN, trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN)), TCNM, HAAs (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA), bromodichloroacetic (BDCAA), chlorodibromoacetic acid (CDBAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), tribromoacetic acid (TBAA), trichloroacetic acid (TCAA)) and the internal standards, 2-bromofluorobenzene and 1,2,3-trichloropropane, were obtained from Sigma-Aldrich. All other reagents were reagent grade.

Preparation and characterization of SMPs

Activated sludge was collected from an aeration tank in a municipal wastewater treatment plant, and cultivated in a laboratory-scale reactor. Initial biomass concentration was kept at about 2,000 mg/L. Glucose (800 mg/L) was utilized as the sole carbon source, as it could be biodegraded completely leaving only SMPs as the remaining organics in the solution (Liu *et al.* 2014). The other synthetic influents were as follows according to our previous study (in mg per L): (NH₄)₂SO₄ (189), KH₂PO₄ (35) (chemical oxygen demand (COD_{Cr}):N:P ratio of 100:5:1), CaCl₂ (0.37), MgSO₄ (5.07), MnCl₂ (0.27), ZnSO₄ (0.44), FeCl₃ (1.45), CuSO₄ (0.39), CoCl₂ (0.42), Na₂MoO₄ (1.26) (Zhang *et al.* 2015). The reactor was operated for 6 h at 25 °C with a precipitation time of 30 min. Supernatant was then collected and filtered through a 0.45 μm filter paper. The filtrate was defined as SMPs.

The characteristics of the SMPs were determined. Dissolved organic carbon (DOC) was measured using a total organic carbon (TOC) analyzer (TOC-VCH, Shimadzu, Japan). Based on theoretical conversion, 1 g glucose is equivalent to 1.067 g COD_{Cr}. Therefore, the concentration of glucose can be measured as COD_{Cr}. The concentrations of glucose (measured as COD_{Cr}), total nitrogen (TN), ammonia nitrogen (NH₄⁺-N), nitrite nitrogen (NO₂⁻-N), and nitrate nitrogen (NO₃⁻-N) were determined using a DR2800 analyzer (HACH, USA). UV₂₅₄ absorption was analyzed with a visible spectrophotometer (UV7595, Shanghai). Bromide was measured with ion chromatography (Dionex DX-600, German). The parameters of the obtained SMPs were as follows: Glucose (measured as COD_{Cr}) = none, DOC = 20.4–25.2 mg/L, UV₂₅₄ = 0.042–0.058 cm⁻¹, TN = 12.4–15.0 mg/L,

NH₄⁺-N = 2.9–3.3 mg/L, NO₂⁻-N = 0.117–0.133 mg/L, NO₃⁻-N = 1.9–2.6 mg/L. These parameters of SMPs were generally constant in different batches.

In addition, SMPs were also collected from two real domestic wastewater treatment plants of Nanjing. The parameters of SMPs were as follows: DOC = 21.5–23.2 mg/L, UV₂₅₄ = 0.137–0.179 cm⁻¹, TN = 10.4–11.6 mg/L, NH₄⁺-N = 3.8–4.3 mg/L, NO₂⁻-N = 0.176–0.246 mg/L, NO₃⁻-N = 2.2–3.1 mg/L, Br⁻ = 108.4–112.6 μg/L, respectively.

Disinfection of SMPs

Chlorination, chloramination and ozonation were conducted as previously described (Zhang *et al.* 2015). Briefly, SMPs were chlorinated by adding NaClO (5%). Monochloramine was prepared daily at a Cl/N molar ratio of 0.7:1. Both chlorine and monochloramine solutions were standardized using the N, N-diethylphenylene-1,4-diamine (DPD) colorimetric method before disinfection (SEPA of China 2002). Ozone was produced from extra dry grade oxygen (with a minimum purity of 99.99%) using a WH-H-Y10 ozone-generator (WAOHUANG, China), and the concentration was determined using spectrophotometric methods (Padhye *et al.* 2013).

Chlorination, chloramination and ozonation were conducted in closed glass bottles. During disinfection, the temperature was kept constant by a thermostatic reactor and pH was adjusted with phosphate buffer. After disinfection, the residual chlorine, chloramine and ozone were quenched using Na₂S₂O₃.

In order to compare and understand the formation of DBPs from SMPs under different conditions, DBPs formation potential (DBPFP, except the formation of DBPs under different disinfectant dosage and reaction time conditions) was used. The details of the prepared samples are shown in Table 1. All samples were conducted in duplicate.

Analysis of DBPs

THMs, CSs, HKs, HANs, and TCNM were determined using EPA method 551.1. HAAs were measured according to EPA Method 552.3. All DBPs were detected using a gas chromatography electron capture detector (GC-ECD) (Agilent 6890, USA). The recoveries of DBPs ranged from 82.9% to

Table 1 | Experimental design

Factors	Chlorination	Chloramination	Ozonation
Temperature (°C)	25, 30, 40	25, 30, 40	25, 30, 40
pH	5.0, 7.0, 9.0	6.0, 8.0, 10.0	5.0, 7.0, 9.0
Reaction time	1, 3, 5, 7 (d)	1, 3, 5, 7 (d)	0.5, 2, 12 (h)
Disinfectant dose	0.2, 0.5, 1.0, 2.0 ^a	0.2, 0.5, 1.0, 2.0 ^b	1, 4, 8, 12 (mg/L)
Bromide (mg/L)	0, 0.2, 0.5, 1.0	0, 0.2, 0.5, 1.0	0, 0.2, 0.5, 1.0
Baseline conditions	25 °C, pH = 7, 7d 2.0 ^a , Bromide = none	25 °C, pH = 8, 7d 2.0 ^b , Bromide = none	25 °C, pH = 7, 12h 4 mg/L, Bromide = none

^aMolar ratio of chlorine/dissolved organic carbon (DOC).

^bMolar ratio of chloramine/DOC.

98.8% and the detection limits of DBPs ranged from 0.04 to 0.56 µg/L.

Statistical analysis

The key factors influencing the formation of DBPs in disinfection of SMPs was investigated using a multivariate regression procedure (backward) of SPSS software (Version 17.0) (Hong *et al.* 2015). The DBPs were designated as the dependent variable, and the influence factors (temperature, pH, disinfectant dosage, reaction time and bromide level) were defined as independent variables. The regression placed independent variables into the equation in the order of their partial correlation coefficients with the dependent variable. Thus, the key factors were identified using this process.

RESULTS AND DISCUSSION

Factors affecting DBPFP

Effect of temperature

Figure 1 shows DBPFP levels at three different temperatures. In chlorination, the formation potential of THMs, HAAs and CSs increased significantly ($p < 0.05$), while that of TCNM remained stable with increasing temperature from 25 °C to 40 °C. In chloramination, the significant temperature-dependent increase ($p < 0.05$) was only observed in TCNM, while THMs, HAAs and CSs increased slightly ($p > 0.05$) with increasing temperature. The generation of HKs showed a significant decrease ($p < 0.05$) with increasing temperature and HANs varied at different

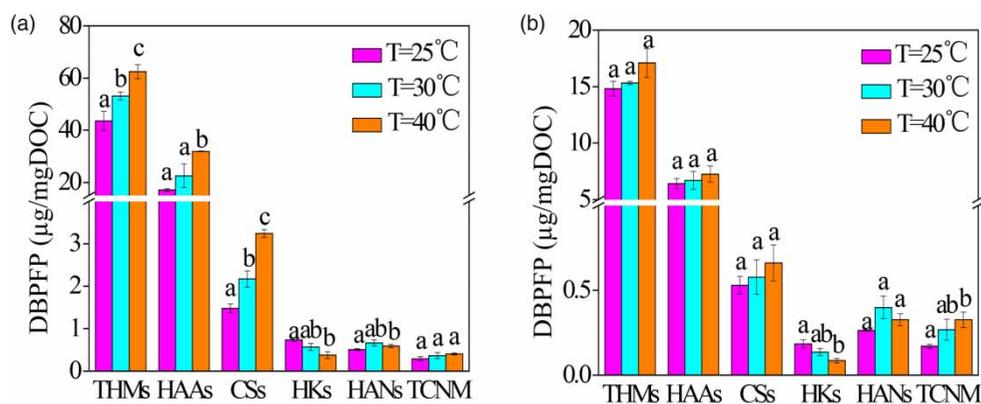


Figure 1 | DBPFP as a function of temperature after chlorination (a) and chloramination (b). Means with the same letter are not significantly different ($p > 0.05$) according to one-way analysis of variance (ANOVA) test (Duncan).

temperatures in both chlorination and chloramination. Similar to the trends of DBPs generated from NOM (Yang *et al.* 2007), if the products are relatively stable (e.g., chloroform and CTC), their formation increased with increasing temperature, however, increasing the temperature may also enhance the decomposition rates of HKs and HANs. Therefore, the concentrations of the unstable DBPs in chlorination and chloramination depend on the relative quantities of their formation and decomposition.

Effect of pH

Figure 2(a) illustrates the DBPFP at pH values from 5.0 to 9.0 in chlorination. Increasing pH significantly increased the formation potential of THMs, CSs and TCNM ($p < 0.05$) but reduced the formation potential of HAAs, HKs and HANs. The results were similar to previous studies (Doederer *et al.* 2014), in which THMs and TCNM levels increased but HAAs level decreased as pH elevated. These results were also reasonable since the alkaline conditions can facilitate the hydrolysis reactions of HKs and HANs to form THMs.

In chloramination, the formation of all the DBPs decreased with increasing pH (Figure 2(b)). The trends of DBPFP were the same as that with NOM as DBPs precursor (Hong *et al.* 2013). This may be because the main factor which affected the formation of DBPs was not the precursor, but the speciation profile of the disinfectant. The pH affected the speciation of chloramines and the hydrolysis of monochloramine to form free chlorine, which has been

suggested to play a significant role in DBPs formation. Under alkaline conditions, monochloramine was the dominant (pH=8) or the only (pH=10) species and its hydrolysis to free chlorine was reduced with increasing pH (Morris & Isaac 1983; Yang *et al.* 2007). This led to the decreasing formation of THMs and CSs with increasing pH. In addition, pH affects the stability of non-THMs DBPs. Their net formation (production minus decomposition) was reduced at a higher pH due to the base-catalyzed decomposition (Reckhow *et al.* 2001). At pH 6, monochloramine and dichloramine coexisted but dichloramine became the dominant species. Although dichloramine was proved to produce less DBPs than monochloramine, there was a fast formation rate and slow decomposition rate of DBPs at this pH (Yang *et al.* 2007). Moreover, some DBPs underwent base-catalyzed decomposition at alkaline pH but remained stable at acidic pH.

Effect of disinfectant dose

Figure 3 illustrates DBPs levels with different molar ratios of disinfectant/DOC. Although the formation of THMs, HAAs, CSs and TCNM were less affected by increasing monochloramine dose than by increasing chlorine dose, the same as with NOM and amino acids as precursors (Yang *et al.* 2012; Hong *et al.* 2013), they all showed generally upward trends as the disinfectant dose increased. This may be because some intermediate DBPs are formed during chlorination and chloramination, which can further react with chlorine or chloramine and result in

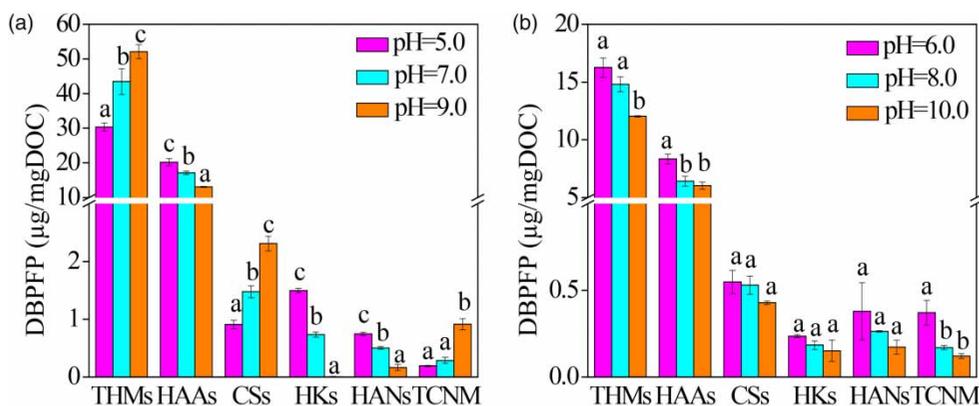


Figure 2 | DBPFP as a function of pH after chlorination (a) and chloramination (b). Means with the same letter are not significantly different ($p > 0.05$) according to one-way ANOVA test (Duncan).

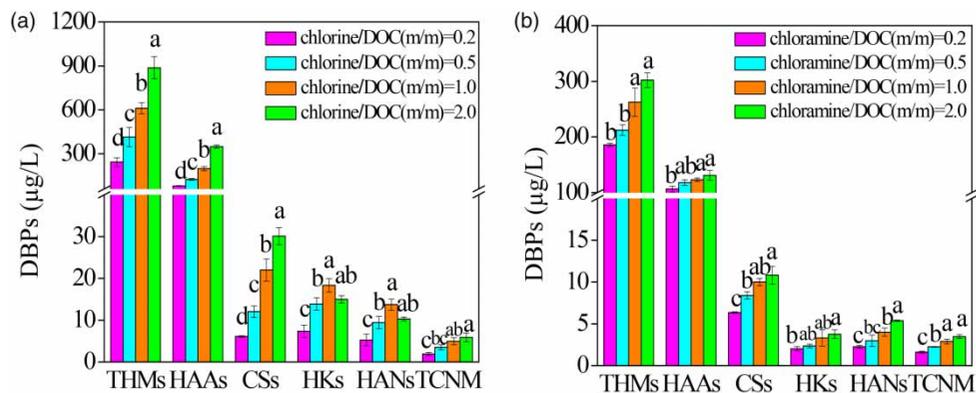


Figure 3 | DBPs concentration as a function of disinfectant dosage after chlorination (a) and chloramination (b). Means with the same letter are not significantly different ($p > 0.05$) according to one-way ANOVA test (Duncan).

the formation of downstream products such as THMs, HAAs and TCNM (Hong *et al.* 2013). However, the formation of HKs and HANs showed different trends with increasing disinfectant dose in chlorination and chloramination. This difference can be attributed to the stabilities of HKs and HANs in the presence of monochloramine, but they may undergo hydrolysis and decomposition in the presence of free chlorine (Reckhow *et al.* 2001; Hong *et al.* 2013).

Effect of reaction time

Figure 4 shows the effects of reaction time on the formation of DBPs in chlorination and chloramination. HKs and HANs remained stable or increased in the presence of monochloramine but underwent hydrolysis and decomposition in the presence of free chlorine (Reckhow

et al. 2001). The formation of THMs, HAAs and CSs increased significantly ($p < 0.05$) as the chlorination time prolonged, but generally remained stable with increasing reaction time in chloramination. These results suggested that chloramine could be a really good alternative disinfectant to chlorine to control the amount of THMs, HAAs and CSs. However, this situation is not applicable to HANs and TCNM. The HANs and TCNM level increased sharply ($p < 0.05$) as the reaction time prolonged in chloramination, and the formation of HANs and TCNM in chloramination was 52% and 60% of that in chlorination, much higher than that of THMs, HAAs and CSs. This result was consistent with previous studies on amino acids, which indicated that chloramine could significantly decrease the formation of regulated DBPs, but could also generate a great many HANs and TCNM (Luo *et al.* 2012; Yang *et al.* 2012).

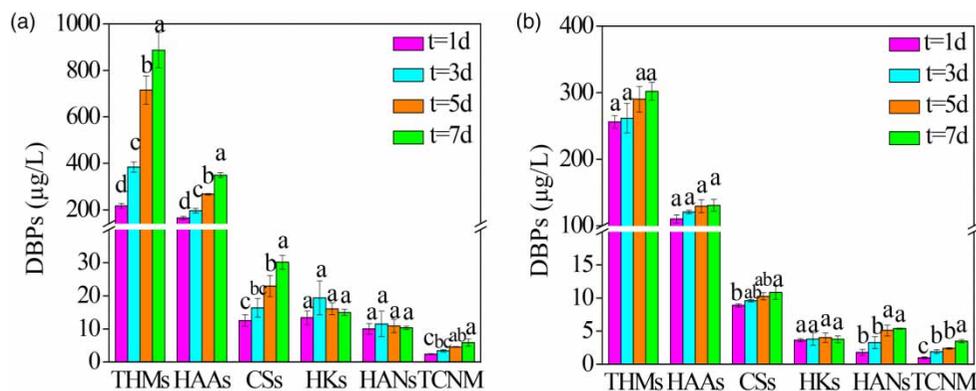


Figure 4 | DBPs concentration as a function of reaction time from chlorination (a) and chloramination (b). Means with the same letter are not significantly different ($p > 0.05$) according to one-way ANOVA test (Duncan).

Effect of bromide level

The effect of bromide level on the total DBPFP was studied by performing experiments at four bromide levels (0, 0.2, 0.5, 1.0 mg/L, Figure 5). Bromine-substituted HKs were not analyzed due to the lack of standards in this study, the presence of bromide ions led to the formation of Br-DBPs including Br-THMs, Br-HAAs and Br-HANs. The total formation potential of THMs and HAAs significantly increased with increasing bromide concentration but that of HANs decreased in both chlorination and chloramination (Figure 5(a) and 5(c)). In addition, with increasing the bromide level, the proportion of Br-DBPs increased (Figure 5(b) and 5(d)) while the formation of chlorine-containing DBPs (Cl-DBPs) including CSs, HKs and TCNM decreased (Figure 5(a) and 5(c)). This may be because bromide ions can be oxidized by free chlorine to hypobromous acid (HOBr), which exhibits much more powerful substitution ability than hypochlorous acid

(HOCl) (Symons et al. 1993). In chloramination, chloramine was unstable and could react with bromide ions to form dibromamine and bromochloramine (Le Roux et al. 2012). Because of the higher nucleophilicity and reactivity of dibromamine and bromochloramine, the incorporation of bromine into DBPs was easier than that of chlorine.

Ozonation did not produce halogenated DBPs in the above experiments. However, Br-THMs and Br-HAAs were produced in the presence of bromide, and their formation potential increased significantly ($p < 0.05$) as the bromide level increased (Figure 5(e)). This is because bromide ions can be oxidized by ozone or hydroxyl radicals to form HOBr, a more effective halogen-substituting agent, thus resulting in increased concentrations of Br-DBPs (von Gunten et al. 2010; Zimmermann et al. 2011).

To better assess the extent of bromine substitution of DBPs, BIF was calculated (Table 2). In agreement with previous studies on NOM (Hu et al. 2010; Hong et al. 2013), the BIF values all presented a similar increasing pattern with

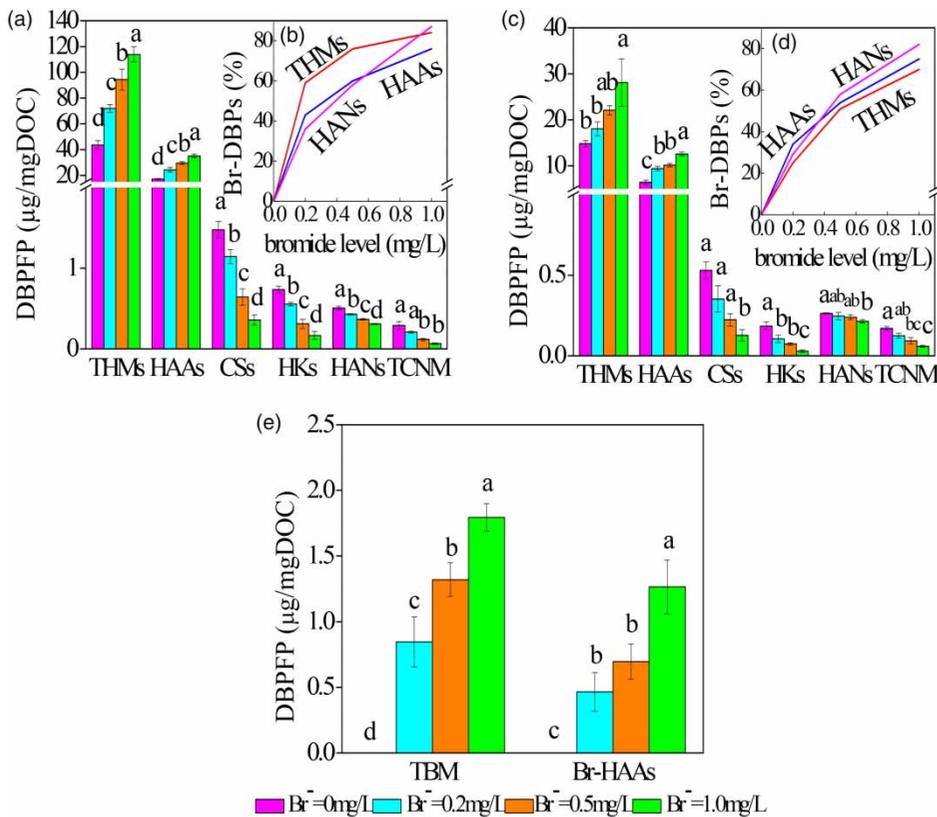


Figure 5 | DBPFP as a function of bromide level after chlorination (a), (b), chloramination (c), (d) and ozonation (e). Means with the same letter are not significantly different ($p > 0.05$) according to one-way ANOVA test (Duncan).

Table 2 | BIF for DBPs as a function of bromide level in chlorination, chloramination and ozonation

Br ⁻ (mg/L)	Chlorination			Chloramination			Ozonation	
	THMs	HAAs	HANs	THMs	HAAs	HANs	THMs	HAAs
0.2	0.69	0.45	0.35	0.24	0.32	0.29	3.00	1.42
0.5	1.05	0.66	0.63	0.56	0.54	0.61	3.00	1.57
1.0	1.29	0.88	1.06	0.96	0.83	1.00	3.00	1.68

BIF was defined as the ratio of the molar concentration of bromine incorporated into a given class of DBPs to the molar concentration of DBPs in that class. Take THMs as an example, BIF_{THMs} is the molar amount of bromine in the THMs ($CHBrCl_2 + 2CHClBr_2 + 3CHBr_3$) divided by total molar THMs concentration: $BIF = (CHBrCl_2 + 2CHClBr_2 + 3CHBr_3) / \Sigma THMs$.

increasing bromide level in chlorination, chloramination and ozonation (except TBM), implying that dibromo-DBPs and tribromo-DBPs were more easily formed with higher bromide levels. Also, BIF values were generally higher in chlorination than in chloramination. The main reason for this may be that compared with chloramine, free chlorine was a stronger oxidant and reacted with bromide faster, thus resulting in greater HOBr formation (Chang *et al.* 2000; Hong *et al.* 2013). Therefore, for wastewater disinfection, chloramination may be a better choice to control the formation of Br-DBPs.

Key factors affecting DBPs formation

The results of key factors affecting DBPs formation from SMPs in chlorination and chloramination are shown in Table 3. Generally, the higher the partial correlation coefficients, the more important the factor is. For THMs, HAAs and CSs formation, bromide level was the most important

factor during both chlorination and chloramination. As for HKs, HANs and TCNM formation, effects of pH and then bromide level were generally more significant than those of other factors during chlorination. During chloramination, bromide level showed the most important influence on HKs formation, but less influence on HANs and TCNM formation. Therefore, it is concluded that reducing bromide level will be an effective strategy to control C-DBPs formation from SMPs, whether for chlorination or chloramination. Besides the bromide level, controlling the pH was also very important to control N-DBPs formation.

DBPs speciation and formation from different disinfection methods and real wastewater

Figure 6 shows DBPs species and concentrations under different disinfection methods without (A) and with (B, Br⁻ = 0.5 mg/L) bromide. Ozonation could produce bromine-containing THMs (Br-THMs, including TBM) and

Table 3 | Results of regression procedure for DBPs

DBPs	Disinfectant	Temperature	pH	Dosage	Reaction time	Bromide level	Regression coefficients	p values
THMs	Chlorine	0.627	0.622	0.887	0.885	0.965	0.951	<0.05
	Chloramine	0.857	-0.912	0.856	0.974	0.995	0.991	<0.01
HAAs	Chlorine	0.923	-0.659	0.871	0.935	0.956	0.959	<0.05
	Chloramine		-0.731	0.770	0.811	0.960	0.943	<0.01
CSs	Chlorine	0.977	0.940	0.936	0.962	-0.958	0.977	<0.01
	Chloramine	0.795	-0.527		0.741	-0.946	0.898	<0.05
HKs	Chlorine	-0.717	-0.937		0.606	-0.866	0.877	<0.05
	Chloramine	-0.848	-0.706		0.836	-0.944	0.877	<0.05
HANs	Chlorine		-0.805		0.563	-0.666	0.667	<0.05
	Chloramine	0.517	-0.434	0.566	0.573	-0.219	0.828	<0.05
TCNM	Chlorine		0.858	0.730	0.739	-0.779	0.771	<0.05
	Chloramine	0.777	-0.872	0.856	0.796	-0.840	0.876	<0.01

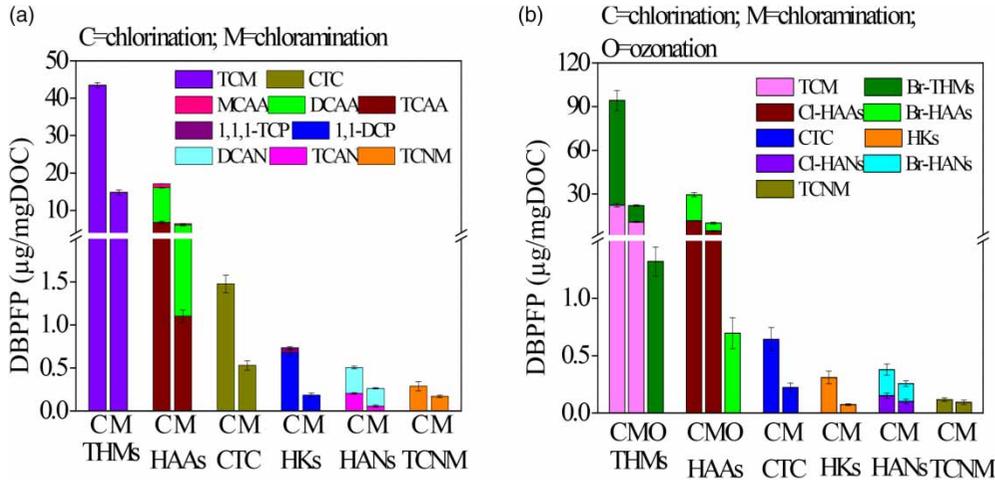


Figure 6 | DBPs species and concentrations upon different disinfection methods with (b, $\text{Br}^- = 0.5 \text{ mg/L}$) or without (a) bromide under baseline conditions (Table 1).

bromine-containing HAAs (Br-HAAs, including MBAA, DBAA and TBAAs) only in the presence of bromide. The DBPs species of chlorinated SMPs and chloraminated SMPs were almost the same either with or without bromide, however, more C-DBPs (THMs, HAAs, CSs, and HKs) and N-DBPs (HANs and TCNM) were formed in chlorination than chloramination. The formation potential of THMs, HAAs, CSs, HKs, HANs and TCNM in chloramination was only 35%, 37%, 36%, 25%, 52%, 60% (without bromide) and 23%, 34%, 35%, 24%, 65%, 80% (with bromide) of those in chlorination, respectively. Moreover, the proportions of Br-THMs/THMs, Br-HAAs/HAAs and Br-HANs/HANs in chloramination

(51%, 54%, 80%) were lower than those found in chlorination (77%, 60%, 89%). Therefore, for wastewater disinfection, chloramination may be not only a good alternative to chlorination in terms of C-DBPs and N-DBPs (HANs and TCNM), but also a better choice to control the formation of Br-DBPs.

In addition, SMPs from two real domestic wastewater treatment plants (A and B) were also disinfected by chlorine, chloramine and ozone (Figure 7). The DBPs species and concentrations formed by SMPs from synthetic wastewater and the real wastewater were almost the same, and THMs were the dominant DBPs species, followed by HAAs, CTC, HKs and N-DBPs (HANs and TCNM).

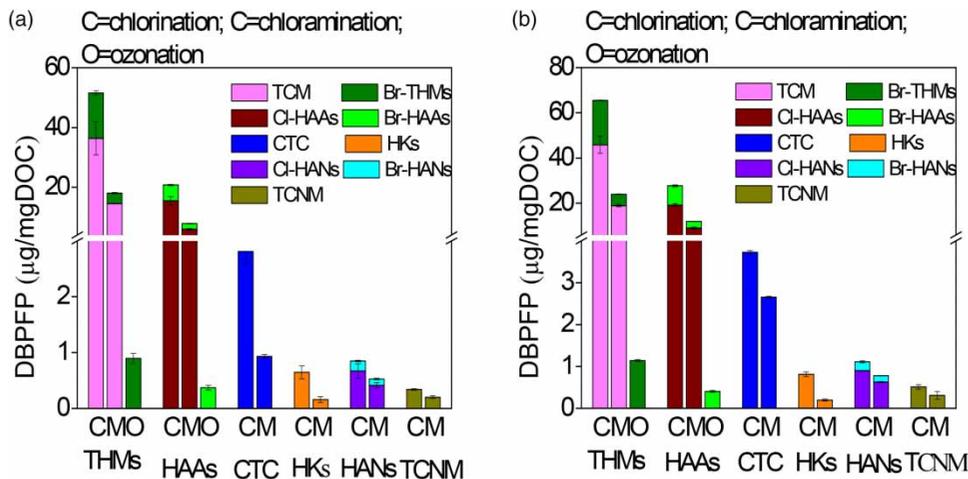


Figure 7 | DBPFP of two real domestic wastewater treatment plants (a and b) upon different disinfection methods under baseline conditions (Table 1).

DBPs formation from SMPs and NOM

For both chlorinated and chloraminated SMPs, the amount of DCAA was higher than that of TCAA, which is distinct from the typical speciation profile of HAAs formed by NOM, which yields much more TCAA than DCAA (Hua & Reckhow 2007). The formation potentials of C-DBPs and N-DBPs were much higher (about two times) than those formed from NOM (Hong *et al.* 2013), this may be because of the higher portion of low molecular weight (MW) hydrophobic acids of SMPs, which was associated with DBPs formation (Chang *et al.* 2001). Moreover, the N-DBPs fraction of the DBPs formed from SMPs (1.3% for chlorination and 1.9% for chloramination, Figure 6(a)) was also higher than that of the DBPs from NOM and humic substances (both less than 0.5%) (Liu & Li 2010; Hong *et al.* 2013), probably due to the higher organic nitrogen content of SMPs (Dotson *et al.* 2009).

Additionally, the main factor which affected N-DBPs formation of SMPs was also distinct from that of NOM reported by Hong *et al.* (2013), in which bromide showed the most important influence on both C-DBPs and N-DBPs. The reason for this may be that (1) the species of studied N-DBPs was different (HNMs for NOM, HANs and TCNM for SMPs) and (2) the precursors of N-DBPs in NOM and SMPs were different.

CONCLUSIONS

C-DBPs and N-DBPs were investigated during chlorination, chloramination and ozonation of SMPs from synthetic and real wastewater. Chloramine rather than chlorine generally resulted in lower formation of C-DBPs, N-DBPs and Br-DBPs. Ozonation could only generate TBM and Br-HAAs in the presence of bromide. The effects of different factors on the formation of DBPs resulting from SMPs were similar to those from NOM. However, SMPs generated more DCAA and N-DBPs, and higher DBFP than NOM. Moreover, reducing the bromide level and controlling the pH could effectively reduce the formation of DBPs from SMPs, either for chlorination or chloramination.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from Natural Science Foundation of Jiangsu Province (Nos. BK2011032, BK20131271), National Natural Science Foundation of China (No. 20777032), and National Hightech R&D Program of China (Grant No. 2013AA06A309).

REFERENCES

- Chang, E. E., Lin, Y. P. & Chiang, P. C. 2001 Effects of bromide on the formation of THMs and HAAs. *Chemosphere* **43**, 1029–1034.
- Doederer, K., Gernjak, W., Weinberg, H. S. & Farré, M. J. 2014 Factors affecting the formation of disinfection by-products during chlorination and chloramination of secondary effluent for the production of high quality recycled water. *Water Research* **48** (1), 218–228.
- Dotson, A., Westerhoff, P. & Krasner, S. W. 2009 Nitrogen enriched dissolved organic matter (DOM) isolates and their affinity to form emerging disinfection by-products. *Water Science and Technology* **60** (1), 135–143.
- Hong, H. C., Xiong, Y. J., Ruan, M. Y., Liao, F. L., Lin, H. J. & Liang, Y. 2013 Factors affecting THMs, HAAs and HNMs formation of Jin Lan Reservoir water exposed to chlorine and monochloramine. *Science of the Total Environment* **444**, 196–224.
- Hong, H. C., Qian, L. Y., Ruan, M. Y., Xiong, Y. J., Xiao, Z. Q., Lin, H. J. & Yu, H. Y. 2015 Use of multiple regression models to evaluate the formation of halonitromethane via chlorination/chloramination of water from Tai Lake and the Qiantang River, China. *Chemosphere* **119**, 540–546.
- Hu, J., Song, H. & Karanfil, T. 2010 Comparative analysis of halonitromethane and trihalomethane formation and speciation in drinking water: the effects of disinfectants, pH, bromide, and nitrite. *Environmental Science & Technology* **44**, 794–799.
- Hua, G. H. & Reckhow, D. A. 2007 Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size. *Environmental Science & Technology* **41** (9), 3309–3315.
- Hua, G. H. & Reckhow, D. A. 2012 Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. *Water Research* **46**, 4208–4216.
- Le Roux, J., Gallard, H. & Croué, J. P. 2012 Formation of NDMA and halogenated DBPs by chloramination of tertiary amines: the influence of bromide ion. *Environmental Science & Technology* **46**, 1581–1589.
- Liu, J. L. & Li, X. Y. 2010 Biodegradation and biotransformation of wastewater organics as precursors of disinfection byproducts in water. *Chemosphere* **81** (9), 1075–1083.

- Liu, J. L., Li, X. Y., Xie, Y. F. & Tang, H. 2014 Characterization of soluble microbial products as precursors of disinfection byproducts in drinking water supply. *Science of the Total Environment* **472**, 818–824.
- Luo, Q., Wang, D. H. & Wang, Z. J. 2012 Occurrences of nitrosamines in chlorinated and chloraminated drinking water in three representative cities, China. *Science of the Total Environment* **437**, 219–225.
- Morris, J. C. & Isaac, R. A. 1983 A critical review of kinetic and thermodynamic constants for the aqueous chlorine-ammonia system. In: *Water Research*, 1st edn (R. L. Jolley, W. A. Brungs, J. A. Cotruvo, R. B. Cumming, J. S. Mattice & V. A. Jacobs, eds). Elsevier-Ann Arbor Science Publishers, Ann Arbor, USA, pp. 49–62.
- Ni, B. J., Raymond, J. Z., Fang, F., Xie, W. M., Sheng, G. P. & Yu, H. Q. 2010 Fractionating soluble microbial products in the activated sludge process. *Water Research* **44**, 2292–2302.
- Padhye, L. P., Kim, J. H. & Huang, C. H. 2013 Oxidation of dithiocarbamates to yield N-nitrosamines by water disinfection oxidants. *Water Research* **47** (2), 725–736.
- Plewa, M. J., Wagner, E. D., Muellner, M. G., Hsu, K. M. & Richardson, S. D. 2008 Comparative mammalian cell toxicity of N-DBPs and C-DBPs. In: *Journal of the American Chemical Society*, 1st edn (T. Karanfil, S. W. Krasner, P. Westerhoff & Y. Xie, eds). ACS Publications-American Chemical Society, New York, USA, pp. 36–50.
- Reckhow, D. A., Platt, T. L., MacNeill, A. L. & McClellan, J. N. 2001 Formation and degradation of dichloroacetonitrile in drinking waters. *Journal of Water Supply Research and Technology-Aqua* **50**, 1–13.
- Roccaro, P., Korshin, G. V., Cook, D., Chow, C. W. K. & Drikas, M. 2014 Effects of pH on the speciation coefficients in models of bromide influence on the formation of trihalomethanes and haloacetic acids. *Water Research* **62** (7), 117–126.
- SEPA of China 2002 *Water and Wastewater Monitoring Methods*, 4th edn. China Environmental Science Press, Beijing, China.
- Symons, J. M., Krasner, S. W., Simms, L. A. & Scimanti, M. 1993 Measurement of THM and precursor concentrations revisited: the effect of bromide ion. *Journal American Water Works Association* **85**, 51–62.
- von Gunten, U., Salhi, E., Schmidt, C. K. & Arnold, W. A. 2010 Kinetics and mechanisms of N-nitrosodimethylamine formation upon ozonation of N-N-dimethylsulfamide containing waters: bromide catalysis. *Environmental Science & Technology* **44**, 5762–5768.
- Yang, X., Shang, C. & Westerhoff, P. 2007 Factors affecting formation of haloacetonitriles, halo ketones, chloropicrin and cyanogen halides during chloramination. *Water Research* **41**, 1193–1200.
- Yang, X., Shen, Q., Guo, W., Peng, J. & Liang, Y. 2012 Precursors and nitrogen origins of trichloronitromethane and dichloroacetonitrile during chlorination/chloramination. *Chemosphere* **88**, 25–32.
- Zhang, B. B., Xian, Q. M., Yang, G., Gong, T. T., Li, A. M. & Feng, J. F. 2015 Formation potential of N-nitrosamines from soluble microbial products (SMPs) exposed to chlorine, chloramine and ozone. *RSC Advances* **5**, 83682–83688.
- Zimmermann, S. G., Wittenwiler, M., Hollender, J., Krauss, M., Ort, C., Siegrist, H. & von Gunten, U. 2011 Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: micropollutant oxidation, by-product formation and disinfection. *Water Research* **45** (2), 605–617.

First received 1 June 2016; accepted in revised form 12 September 2016. Available online 4 November 2016