Effects of ozonation and biological filtration on the formation of nitrogenous disinfection byproducts during chloramination

Yi-Hsueh Chuang and Hsin-hsin Tung

ABSTRACT

This study investigates the formation potential (FP) of nitrogenous disinfection byproducts and haloacetic acids (HAAs) during ozonation and biofiltration. Ozonation of raw waters was performed in batches with 1 mg O_3/mg dissolved organic carbon (DOC). The ozonized waters were subsequently passed through a biofilter with 25 minutes of empty bed contact time. The results show that the increases of biodegradable DOC in hydrophobic fractions were higher than those in hydrophilic (HPI) or transphilic fractions. Ozonation reduced the DOC (<10%), and FPs of haloacetonitriles (HANs) and HAAs by 23–70%. Subsequent biofiltration removed up to 35% of DOC, whereas the additional removals of HAN and HAA FPs were negligible during biofiltration. Trichloronitromethane FPs tended to increase by a factor of 5–10 after ozonation and slightly decrease (15–20%) during biofiltration. In the two nitrogen-rich natural organic matters (NOMs), transphilics and HPIs constituted half of the organic carbons and contributed 64–70% of the total N-nitrosodimethylamine (NDMA) formation. Ozonation-biofiltration reduced NDMA precursors in these two water sources but significantly enhanced NDMA formation in Suwannee River NOM. The increase of NDMA formation was attributable to the alteration of NOM characteristics of the HPI fraction by ozonation; the NDMA FP increased 214% in the HPI fraction after ozonation.

Key words | biofiltration, haloacetonitriles, N-nitrosodimethylamine, ozonation, trichloronitromethane

Yi-Hsueh Chuang
Hsin-hsin Tung (corresponding author)
Graduate Institute of Environmental Engineering,
National Taiwan University,
No. 1, Sec. 4, Roosevelt Rd,
Taipei 106,
Taiwan
E-mail: *htung@ntu.edu.tw*

INTRODUCTION

In natural waters, frequent algal blooms may increase dissolved organic nitrogen (DON), which leads to the formation of disinfection byproducts (DBPs) during water chlorination and/or chloramination (Lee *et al.* 2007b). In particular, DON has been reported to be an important precursor for nitrogenous DBPs (N-DBPs), including haloacetonitriles (HANs), halonitromethanes (HNMs), and *N*-nitrosodimethylamine (NDMA) (Lee *et al.* 2007b). The levels of these N-DBPs in drinking water, ranging from low ng/L (e.g., NDMA) to low μg/L (e.g., HANs and HNMs), are orders of magnitude lower than those of commonly regulated trihalomethanes (THMs) and haloacetic acids (HAAs) (Krasner *et al.* 2006; Richardson *et al.* 2007). Although their levels in drinking water are low, the genotoxicity and cytotoxicity of these N-DBPs are much higher than those of THMs and HAAs (Plewa *et al.* 2004), which may raise health concerns.

Due to its hydrophilic (HPI) nature, DON is not easy to remove during conventional treatment processes (Lee *et al.* 2006) and may be transformed to N-DBPs in subsequent chlorination or chloramination. Alternatively, ozonation combined with biofiltration has been used to eliminate the DBP precursors. Ozonation alters the characteristics of natural organic matter (NOM) and may reduce or promote

the formation of DBPs. Although studies have shown that ozonation of bulk dissolved organic matter (DOM) prior to chlorination or chloramination reduced the formation potentials (FPs) of HANs and NDMA (Chen & Valentine 2008) and increased those of HNMs in water (Hoigné & Bader 1988; Chiang et al. 2010; Hu et al. 2010), the effects of ozonation on the changes in N-DBPFP from different organic fractions are not clear. Using amino acids or amines as the model compounds, previous studies have reported that ozonation may convert amines into nitroalkanes and enhance the formation of trichloronitromethane (TCNM) during chlorination and/or chloramination (Shan et al. 2012). Ozonation may also promote nitrile formation from the reaction between ozonation-induced aldehydes and inorganic chloramines (Joo & Mitch 2007). Therefore, the increases in HAN and HNM FPs may be pronounced in organic fractions with high DON concentrations, which likely contain many amino acid precursors.

Ozonation transforms hydrophobic substances into aliphatic and carboxyl carbon (Westerhoff et al. 1999; Galapate et al. 2001; Karnik et al. 2005) and enhances the biodegradability of NOM. Maximal conversion of dissolved organic carbon (DOC) to biodegradable DOC (BDOC) occurs at a ratio of 1 mg O_3/mg DOC (Siddiqui et al. 1997). Of the ozonation-induced BDOC, only a small portion is attributable to aldehydes and short-chain carboxylic acids and over 60% are not well characterized (Richardson et al. 2002; Swietlik et al. 2004). In addition, little work has been done to explore the relationship between biofiltration-removable DOC and the N-DBP FPs. Therefore, the objective of this study is to explore the changes in the formation concentrations of HAN, TCNM, and NDMA, which are three groups of N-DBPs associated with chloramination of water, during ozonation and biofiltration.

MATERIALS AND METHODS

Water sources and fractionation

In this study, three DOM sources isolated from surface waters were investigated. Surface water 'ST' was collected from a local eco-pond. 'TH' was collected from a water reservoir with frequent algal blooms. A model DOM, Suwannee River NOM (SRN, RO isolation, Cat. #1R101N), was purchased from the International Humic Substance Society. XAD7HP and XAD4 resins were used to separate DOM into the following six fractions based on hydrophobicity and functional groups: hydrophobic acid (HPOA), hydrophobic base (HPOB), hydrophobic neutral (HPON), transphilic acid (TPIA), transphilic neutral (TPIN), and HPI. The characteristics of the DOM fractions, the fractionation results, and the fractionation method are described elsewhere (Chuang et al. 2013). The DON to DOC ratios were 0.16 for ST, 0.14 for TH, and <0.01 for SRN. The specific ultraviolet absorbance (SUVA) values of these DOMs varied from 1.36 to 3.3 L mg^{-1} cm^{-1} (SRN > ST > TH). The water parameters for DOMs tested in this study are summarized in Table 1.

Experiments

The monochloramine used in DBPFP was freshly prepared before each experiment. Ammonium chloride solution (pH 8.5) was refrigerated (4 °C) for 1 h. Sodium hypochlorite (6–14%, Sigma-Aldrich, USA) was added at a molar ratio of 1 NaOCl: 1.2 ammonium chloride to generate a monochloramine concentration of approximately 7,000 mg L^{-1} as Cl_2. A phosphate buffer maintained the desired pH of each DBPFP reaction (10 mM). The DBPFP tests were conducted (headspace-free) with a chloramine dosage of 10.5 mg L^{-1} as Cl_2 (3*(DOC) in mg L^{-1}) (Dotson et al. 2009). The decay of total chlorines was monitored periodically using the N,N-diethyl-p-phenylenediamine colorimetric method (Method 8167, Hach Company, USA). The samples for N-DBP concentration measurements were periodically taken, and residual chlorine was quenched by ascorbic acid. The DBP concentrations were analyzed immediately. Ozonation and biofiltration experiments were not conducted in HPOB due to low organic content in these fractions (Table 1).

During the ozonation experiments, 3.5 mg L^{-1} DOC of organic fractions (5 mM phosphate buffered at pH 7.2) were initially prepared. The ozonation process (25 °C) was achieved by adding small aliquots of O_3 stock (approximately 1 mM O_3), which was produced by continuously bubbling O_3 (CFS-2G, Ozonia, USA) gas into Milli-Q water (Millipore Co., MA, USA) on an ice bath, to the

Table 1 │ DOM constitution and general water parameters of waters

| Waters | SUVA (L m^{-1} mg^{-1}) | DON/DOC | DOM constitution (%) and SUVA (L-m/mg, in parentheses) | | | | | |
| | | | Hydrophobic | | | Transphilic | | Hydrophilic |
			HPOA	HPOB	HPON	TPIA	TPIN	HPI
ST	1.86	0.16	24.6 ± 0.8 (2.83)	1.4 ± 0.3 (NA)	25.7 ± 0.5 (1.21)	5.7 ± 0.4 (0.84)	19.1 ± 0.0 (0.78)	15.1 ± 0.0 (1.33)
TH	1.36	0.14	31.9 ± 0.7 (2.30)	2.7 ± 0.1 (NA)	13.6 ± 4.5 (0.84)	11.5 ± 0.6 (1.36)	8.4 ± 0.2 (0.62)	32.7 ± 2.3 (0.26)
SRN	3.30	<0.01	69.5 (3.79)	2.2 (3.11)	15.1 (2.41)	2.2 (1.42)	8.1 (0.32)	2.7 (1.06)

NA – not measured. Fractionation of DOM was duplicated (n = 2).

samples to achieve a final dosage of 1 mg O_3 mg DOC^{-1}. The ozonated samples were allowed to stand overnight (no ozone residual was detected after the ozonation step). The biofilter consisted of a glass column (30 cm in height and 1.75 cm in width) packed with silica sand, and the biofilm was established by continuously feeding raw water collected from pond water (DOC = 4.7 mg L^{-1}) for over 3 months. Before the biofiltration experiments, 100-mL sample aliquots (~2 bed volumes) were passed through the biofilter and discarded.

Analytical methods

Four HANs (dichloroacetonitrile (DCAN), trichloroacetonitrile, dibromoacetonitrile and bromochloroacetonitrile) and TCNM were analyzed using United States Environmental Protection Agency (USEPA) method 551.1. Chlorinated and brominated HAAs were analyzed by USEPA method 552.3 using gas chromatography with a micro electron capture detector (GC-µECD, 6890N, Agilent Technologies, USA). NDMA was pre-concentrated by solid phase extraction and analyzed by a high performance liquid chromatography tandem mass spectrometer using a positive mode electrospray ionizer (API4000, Applied Biosystems, USA) with multiple reaction monitoring (Chuang *et al.* 2013). The DOC concentration was analyzed using a wet oxidation method with a total organic carbon analyzer (OI-Analytical, Model 1010TOC, College Station, USA). The aqueous ozone concentration was analyzed using Standard Method 4500-O3 (APHA 1998). The bioactivity within the biofilter was confirmed by measuring the adenosine triphosphate (ATP) concentration (ENLITEN® ATP Assay System Bioluminescence Detection Kit, Promega). The ATP concentration of the biofilter was 94 ± 14 pg/mg sand, which agrees with the ATP concentrations found in typical biofilters (Pharand *et al.* 2014). The method used for nitrogen source tracking for the TCNM formed was adapted from a previous study (Chuang & Tung 2015). The typical mass spectrum of TCNM, using electron impact ionization as the ionization source, contains m/z 117, 119, and 121 (CCl_3^+), m/z 82, 84, and 86 (CCl_2^+), m/z 47 ($C^{35}Cl^+$), m/z 49 ($C^{37}Cl^+$), and m/z 46 (NO_2^+) (Montesinos *et al.* 2011). During ^{15}N-monochloramination of organic fractions, m/z 46 is detectable with the presence of ^{14}N-TCNM. By contrast, with the

presence of ^{15}N-TCNM, the intensity of m/z 46, ^{14}NO$_2^+$, is expected to be lower, and the intensity of m/z 47 is expected to be larger due to the existence of ^{15}NO$_2^+$.

Due to the interference of C^{35}Cl$^+$, a fragment of m/z 47, the percentage of ^{15}N-TCNM cannot be determined by the area ratio of m/z 47 (^{15}NO$_2^+$) to m/z 46 (^{14}NO$_2^+$) $+ m/z$ 47. Nevertheless, the area ratios of m/z 46 to m/z 117 were found to be constant (0.1025 ± 0.0007, $n = 4$) in the TCNM standard samples with different concentrations (0.5–10 mg L^{-1} in methyl tert-butyl ether). Therefore, the ^{14}N percentage in the TCNM of samples can be calculated by Equation (1), assuming that a sample comprising 100% ^{14}N-TCNM yields a constant ratio of m/z 46 to m/z 117 (i.e., 0.1025):

$$\frac{\frac{m/z\ 46}{m/z\ 117}_{100\%\ 14N-TCNM}}{\frac{m/z\ 46}{m/z\ 117}_{sample}} = \frac{0.1025}{\frac{m/z\ 46}{m/z\ 117}_{sample}}$$

$$= \frac{100\%\ ^{14}N - TCNM}{x\%\ ^{14}N - TCNM} \quad (1)$$

where x denotes the ^{14}N percentage in TCNM in the samples. By means of Equation (1), the ^{14}N-TCNM formed during chloramination of tyrosine was determined to be 4.3–5.7% of total TCNM, which corresponds to 94.3–95.7% of ^{15}N-TCNM. These percentages agree with data reported by Yang et al. (2012).

RESULTS AND DISCUSSION

HAA and HAN FPs during ozonation and biofiltration

Breaking conjugated double bonds, or depolymerization, is one of the main reactions during the ozonation of DOM (Kleiser & Frimmel 2000; Thomson et al. 2004). Therefore, in the organic fractions tested in this study, ozonation significantly decreased SUVA at 254 nm (SUVA$_{254}$) (59.3–64.9%), though DOC (0–21.5%) experienced less reduction. This result agrees with previous studies (Zhang et al. 2008; Lamsal et al. 2011).

The chloramination of SRN produced higher HAAFP and HANFP than those produced from other DOMs

(Figure 1). In addition, the hydrophobic fractions gave higher HAAFP and HANFP than the corresponding transphilic and HPI fractions (Figures 2 and 3). HPOA, TPIA and TPIN comprise 50.8–86.8% of total DOC in four DOMs. These organic fractions tended to give high HAN and HAA FPs. Therefore, hydrophobic and transphilic fractions are the most important precursor sources for HANs and HAAs in natural NOMs. In the three DOMs tested in this study, the decreases in HANFP and HAAFP caused by ozonation were consistently within similar ranges; these were 38–56% for HANFP and 28–65% for HAAFP (Figure 1). This may be because the majority of precursors of HAA and HAN in natural waters have similar origins (e.g., β-diketone structure within NOM) (Yang et al. 2008).
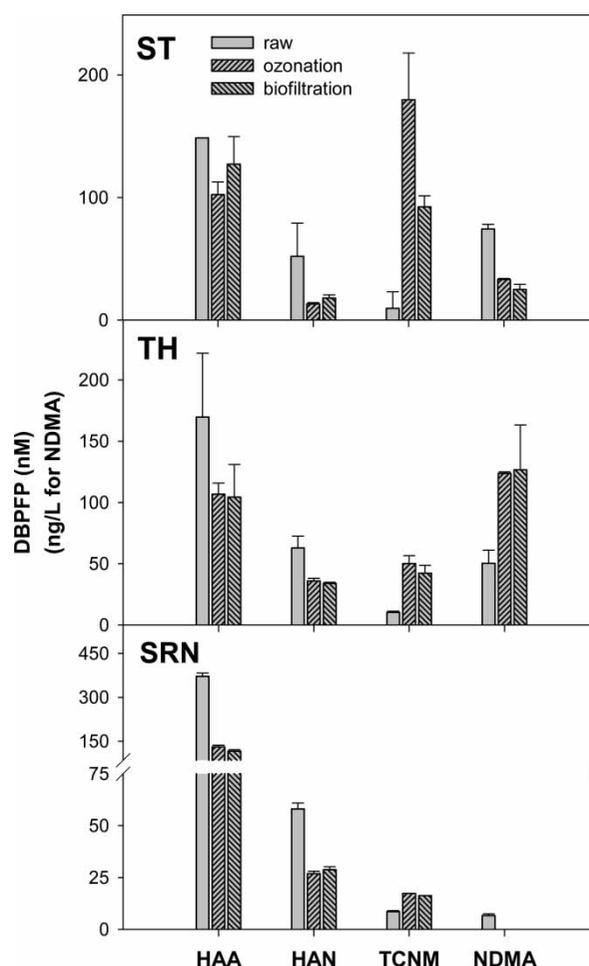

Figure 1 | Effects of ozonation and biofiltration on N-DBPFP of the DOMs tested. The initial DOC was 3.5 mg L^{-1}. The ozone dosage was 3.5 O$_3$ mg L^{-1}. The EBCT of biofiltration was 25 min. Experiments were conducted at room temperature. Error bars represent standard deviations from sample replicates ($n = 2$).
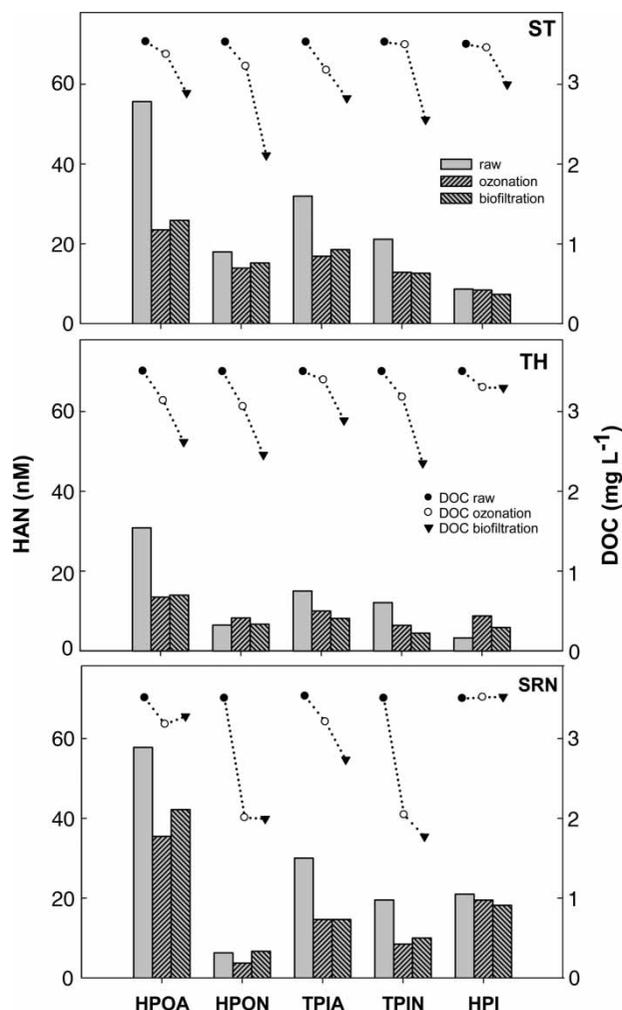
Figure 2 │ Effects of ozonation and biofiltration on HANFP in the organic fractions tested. The initial DOC was 3.5 mg L^{-1}. The ozone dosage was 3.5 O$_3$ mg L^{-1}. The EBCT of biofiltration was 25 min. Bars and dots represent the FP and DOC concentrations, respectively.

Figure 3 │ Effects of ozonation and biofiltration on HAAFP in the organic fractions tested. The initial DOC was 3.5 mg L^{-1}. The ozone dosage was 3.5 O$_3$ mg L^{-1}. The EBCT of biofiltration was 25 min. Bars and dots represent the FP and DOC concentrations, respectively.

Organic fractions with high aromatic contents, as measured by SUVA$_{254}$, are likely rich in β-diketone structure, which is readily destroyed by ozonation (Rice 1980). In this study, the reductions of HANFP and HAAFP by ozonation in HPOA, TPIA and TPIN were greater than those in the other fractions (Figures 2 and 3). The changes in HANFP in HPIs before and after ozonation were negligible, suggesting that HAN precursors in HPI fractions are less reactive toward ozone.

After ozonation, the subsequent biofiltration removed 0.1–34% of DOC. High DOC removal was evident in hydrophobic and transphilic fractions. Note that the HAAFP and the HANF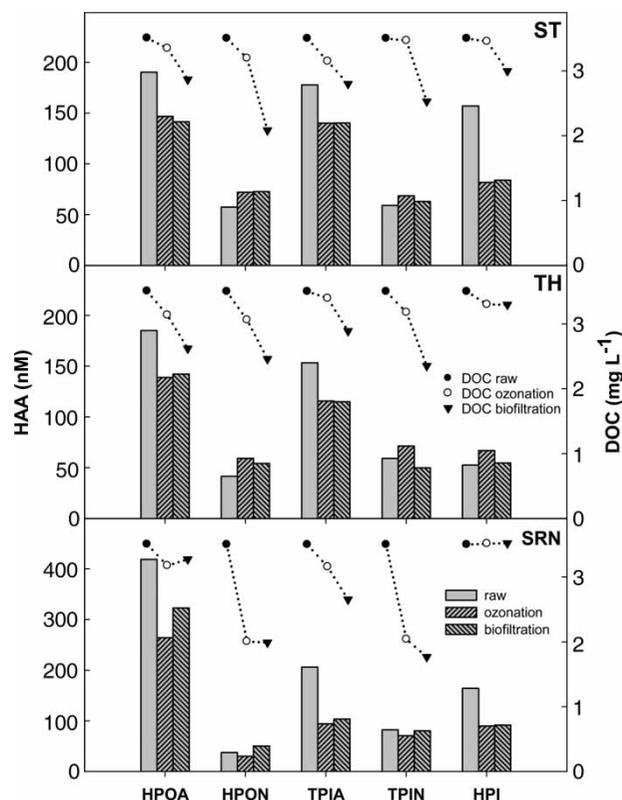P of all organic fractions remained stable before and after biofiltration regardless of DOC removal (Figures 2 and 3). This suggests that the ozonation-induced BDOC in organic fractions is not the major source of HAA or HAN precursors. Increasing the empty bed contact time (EBCT) of biofiltration resulted in greater DOC removal but did not result in HAAFP or HANFP reductions (Figure 4), which supports this hypothesis.

TCNMFP

The TCNMFPs in the three DOMs tested in this study were generally low (approximately 10 nM in 3.5 mg L^{-1} DOC samples) (Figure 1). No apparent correlation was found between the TCNM yields and the DON/DOC of organic fractions (data not shown), which is in agreement with previous studies (Lee *et al.* 2007b; Yang *et al.* 2008). After ozonation, the TCNM chloramination FP in three DOMs increased 5–10 times (Figure 1). Among the DOMs tested
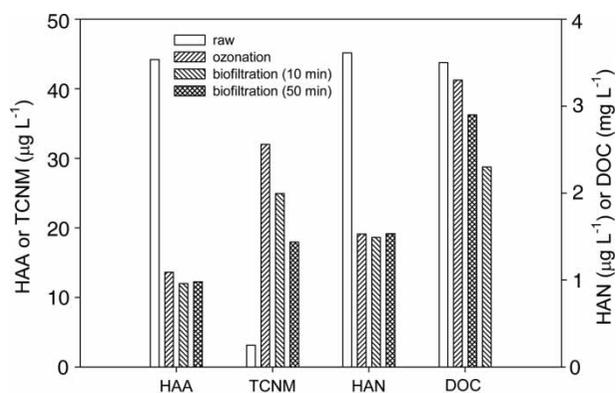
Figure 4 | Changes in DBPFPs and DOC of NOM (ST) during different treatment processes. The initial DOC was 3.5 mg L^{-1}. The ozone dosage was 3.5 O$_3$ mg L^{-1}. The EBCT of biofiltration was 25 min.

in this study, whereas a high TCNM chloramination FP (51 nM/mg DOC) was observed in ozonized ST (Figure 1), the TCNM chloramination FPs in ozonized TH and in ozonized SRN were relatively low (14 nM/mg DOC and 4.8 nM/mg DOC, respectively). Similar observations have been reported previously (Hoigné & Bader 1988; Hu et al. 2010). Hu et al. (2010) reported that the HNM chloramination FP in ozonized waters ranged from not detected to 10.4 nM/mg DOC. In addition, a correlation between HNM FP and DON was reported in ozonized waters; a significant increase in TCNM FP caused by ozonation was found in water with the highest DON concentration (0.27 mg-N/L) (Hu et al. 2010). This suggests that ozonation may transform DON within natural water into HNM precursors that form HNMs upon subsequent chlorination or chloramination. Thus, ST, a DOM with ample DON (i.e., 0.16 mg-N/mg DOC), may be rich in organic substances that are readily transformed into HNM precursors during ozonation. The experimental results in this study show that the elevated TCNMFP in the DOMs tested may be because ozonation transforms organic matters into TCNM precursors in transphilic and HPI fractions (Figure 5). Figure 5 shows that the changes in TCNMFP before and after ozonation were substantial in TPIAs, TPINs, and HPIs, whereas ozonation caused trivial changes in TCNMFP in HPOAs and decreased the TCNMFP in HPONs.

Previous work has demonstrated that the formation of TCNM in drinking water is associated with water ozonation prior to chlorination; switching the order to chlorination
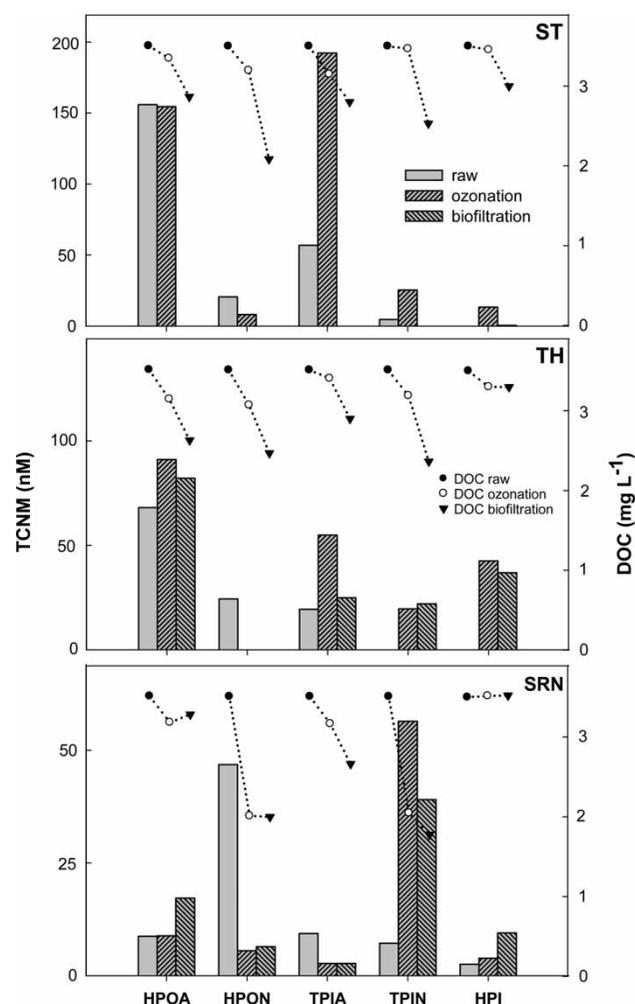

Figure 5 | Effects of ozonation and biofiltration on TCNMFP in organic fractions tested. The initial DOC was 3.5 mg L^{-1}. The ozone dosage was 3.5 O$_3$ mg L^{-1}. The EBCT of biofiltration was 25 min. Bars and dots represent the FP and DOC concentrations, respectively.

followed by ozonation led to negligible concentrations of TCNM formation (Hoigné & Bader 1988). Hypotheses for the roles of ozonation in enhancing TCNM formation have been proposed. Using amino acids as precursors, ozonation converts amino acids into nitro-group-containing compounds (Shan et al. 2012). Transformation of amines into nitrous compounds such as nitromethane and nitrophenol by ozonation is a possible explanation for the elevated TCNM formation (Elmghari-Tabib et al. 1982; Merlet et al. 1985). These proposed pathways indicate that the formation of a nitro group is essential for the formation of TCNM during post-chlorination or post-chloramination, which likely chlorinates the α-carbon of the nitro group

and results in the formation of chlorinated nitroalkanes. However, chlorination prior to ozonation may convert amines into *N*-chloroamines or *N,N*-dichloroamines (Deborde & von Gunten 2008), thus preventing the formation of nitroalkanes. Another possible mechanism for the elevated TCNM is that ozonation of amines produces aldehydes; *N*-chloramine incorporation of monochloramine on aldehydes during chloramination has been demonstrated for TCNM formation (Yang *et al.* 2012), although the importance in authentic waters has not been evaluated. Our results show that by applying ^{15}N-chloramines to track the nitrogen source, the nitrogen origination of TCNM formed after ozonation and post-chloramination was mainly from organic nitrogen (Table 2). Transphilic and HPI fractions were rich in DON compared with hydrophobic fractions and may consist of ample amines. Therefore, ozonation boosting nitro-group formation may be the important mechanism for elevated TCNM formation.

Biofiltration tended to remove the FP of TCNM (Figure 1). Increasing the EBCT of biofiltration lowered the TCNMFP (Figure 4). Recent work (Krasner *et al.* 2012) investigated water treatment plants practicing ozonation followed by granular activated carbon (GAC) filtration and reported that TCNMFP could be removed through GAC, which might involve the mechanisms of adsorption and/or biodegradation. The results of this study indicate that the TCNM precursors produced during ozonation are partially biodegradable.

NDMAFP

Our previous study has shown that transphilic and HPI fractions are the main precursor sources for NDMA in natural waters (Chuang *et al.* 2013). Compared with the NDMAFP in transphilic and HPI fractions, the NDMAFP from the chloramination of hydrophobic fractions was relatively low, (11 ± 2.7 ng/mg DOC, Figure 6). The NDMAFP is correlated with the DON to DOC levels in the transphilic and HPI fractions, which constitute ~40% DOC in the DOMs tested in this study (Chuang *et al.* 2013).

Ozonation decreased the NDMAFP in ST and SRN but increased NDMAFP by 30% in TH, and the following biofiltration removed limited NDMAFP in the NOMs tested in this study (Figure 1). The organic fractions separated from these NOMs responded differently to ozonation; ozonation significantly decreased the NDMAFP for most of the organic fractions, agreeing with a previous study (Lee *et al.* 2007a). A sharp increase of NDMAFP (214%) was evident in TH-HPI (Figure 6), suggesting that ozonation may cause the release of NDMA precursors in TH-HPI.

A previous study has characterized extracellular organic matters (EOM) and intracellular organic matters (IOM) as HPI-rich organic matters using the serial resin fractionation method (Li *et al.* 2012). These algal matters have low SUVA
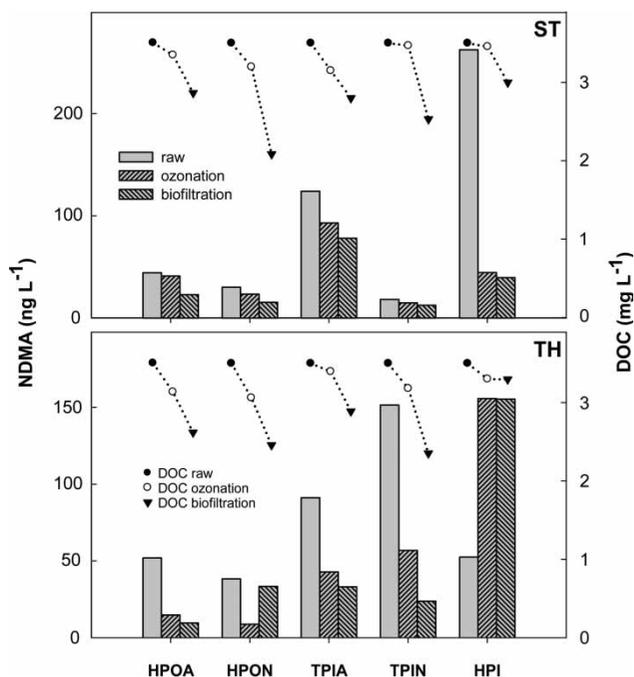
Table 2 | Results of nitrogen source tracking of TCNM formed during 15N-labeled chloramination of pre-ozonized organic fractions

DOM source	Fractions	14N-TCNM percentage	15N-TCNM percentage
ST	HPOA	95%	5%
	HPON	84%	16%
	TPIN	96%	4%
TH	HPOA	96%	4%
	HPON	65%	35%
	HPI	96%	4%
SRN	TPIN	96%	4%

Figure 6 | Effects of ozonation and biofiltration on NDMAFP in the organic fractions tested. The initial DOC was 3.5 mg L^{-1}. The ozone dosage was 3.5 O$_3$ mg L^{-1}. The EBCT of biofiltration was 25 min.

(i.e., 0.4–0.9 L/mg m) and are DON-rich (e.g., DON/DOC = ~0.2) (Henderson *et al.* 2008; Li *et al.* 2012). Studies have demonstrated that pre-ozonation of EOM and IOM, either from algal matters or bacterial cells, likely increases their NDMAFP during subsequent chloramination (Wert & Rosario-Ortiz 2013; Zhou *et al.* 2015). In this study, TH was collected from a water reservoir with frequent algal blooms and that may contain ample EOM and IOM. The EOM and IOM may be fractionated into the HPI during organic matter fractionation, as indicated by an SUVA of TH-HPI of 0.26 and high DON/DOC (0.19). Thus, the increase of NDMAFP in ozonized TH-HPI might be due to the presence of algal EOM and IOM.

IMPLICATIONS

Recent work using isotopically labeled monochloramine ($^{15}NH2Cl$) to track the nitrogen sources of N-DBPs have shown that during chloramination of natural waters, the nitrogen sources of N-DBP could be both DON (^{14}N-DBPs) and inorganic chloramines (^{15}N-DBPs) (Huang *et al.* 2013; Chuang & Tung 2015). In addition, due to the discrepancy of formation kinetics, the formation concentration of N-DBP, where the nitrogen atoms originated from DON (^{14}N-DBPs), tends to be higher than that of N-DBP, where the nitrogen atoms originated from chloramines (^{15}N-DBPs) during conventional chloramination disinfection (Chuang & Tung 2015). Based on FP analysis, previous studies reported that ozonation tended to decrease the formation of DCAN. Our results suggest that the decrease of the FP of DCAN was due to the precursors within hydrophobic fractions rather than within HPI fractions. HPI fractions tend to consist of ample DON, which would likely be rapidly transformed into HAN under typical chloramine disinfection. Therefore, although ozonation-biofiltration is capable of lowering the HANFP, the efficiency of reducing the formation concentration of HAN may be limited under conventional disinfection conditions. In addition, pre-chlorination or pre-chloramination prior to ozonation-biofiltration might be applicable for inactivating the precursors of TCNM, potentially by converting amines to *N*-chloramines.

CONCLUSIONS

This study investigates the FP of N-DBPs, including HANs, TCNM, and NDMA, during ozonation and biofiltration. In the DOMs tested, ozonation significantly removed the HANFP. The reduced HANFP in DOMs can be attributed to the precursor inactivation in the hydrophobic and transphilic fractions, whereas the HAN precursors within the HPI fractions are less reactive with ozone. Ozonation increased TCNMFP, particularly in transphilic and HPI fractions. Nitrogen source tracking indicated that the nitrogen source of the TCNM formed was mainly from organic nitrogen. In addition, ozonation tended to reduce NDMAFP, with the exception of that found in TH-HPI. Although biofiltration removed DOC, the removed DOC was not associated with the precursors of HAA and HAN. The ozonation-induced TCNM precursors were partially biodegradable. Increasing EBCT resulted in a lower TCNMFP.

ACKNOWLEDGEMENTS

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