Effect of pre-ozonation on N-nitrosodimethylamine (NDMA) formation from four drinking-water sources during subsequent chloramination

X. B. Liao, L. Zhao, L. L. Shen, M. Y. Chen, C. Chen, F. Li, B. L. Yuan and X. J. Zhang

ABSTRACT

Ozone has been widely used for water treatment all over the world. This study investigated the effects of pre-ozonation on N-nitrosodimethylamine (NDMA) formation from four drinking-water sources during subsequent chloramination. Moreover, relationships between NDMA and water-quality parameters (dissolved organic carbon (DOC), dissolved organic nitrogen (DON), hydrophobic fractions (HFs), positive-charged fractions (PCFs), ultraviolet absorbance at 254 nm wavelength (UV_{254}), ammonia) were determined. The results indicated that NDMA formed directly by ozonation, but the concentrations (5.7–37.8 ng/L) were much lower than during chloramination (25.3–193 ng/L). Pre-ozonation slightly augmented NDMA formation from reservoirs, while it facilitated NDMA precursor destruction in the lake and river. The river was rich in organic matter, its DOC concentration was up to 4.97 mg/L, while the DON/DOC ratio (4.68%) was low; the lake possessed the most organic nitrogen and highest DON/DOC ratio (10.76%). HFs in reservoir #2 were low (1.27 mg/L), and the HFs/DOC ratio was especially high (73.4%). PCFs constituted 48.5–72.1% of DOC. UV_{254} values were in the range 0.081–0.175 cm^{-1}. The ammonia concentration was high in the lake water (0.29 mg/L), while that in reservoir #2 was only 0.08 mg/L. There was a strong correlation between NDMA formation and the removal of ammonia, DON and PCFs.

Key words | DOC, DON, drinking water sources, NDMA, ozonation

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INTRODUCTION

N-nitrosodimethylamine (NDMA), which is classified as a probable human carcinogen, has widely been detected as an emerging disinfection by-product (DBP) in chloraminated water around the world (Krasner *et al.* 2013). To guarantee the safety of drinking water, NDMA formation control and its precursor's removal are of increasing interest (Krasner *et al.* 2013; Hu *et al.* 2018).

Due to its strong oxidation ability, ozone has been reported to be a highly efficient oxidant to reduce NDMA formation in subsequent chloramination (Liao *et al.* 2014; McCurry *et al.* 2015; Zou *et al.* 2018). Pre-ozonation was also found to be the most effective pretreatment method for NDMA control in drinking-water utilities in the USA (McCurry *et al.* 2015). Both pre- and mid-ozonation achieved more than 30% net removal of NDMA precursors when treating agricultural wastewater-impacted lake water (Liao *et al.* 2014). However, direct NDMA formation from typical model precursors during ozone treatment has been found in recent years (Marti *et al.* 2015). In addition, NDMA has also been frequently detected in finished water in many countries, which might be attributed to the use of ozone for the disinfection or pre-oxidation of drinking water (Asami *et al.* 2009; Chen *et al.* 2018). The contradictory results indicate that ozone can either deactivate specific

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precursors or convert them into precursors with higher NDMA yields. It is imperative for us to improve our knowledge about the relationships between ozone and the water-quality parameters for NDMA formation in drinking-water sources.

Because of the fact that source water pollution is serious in many countries, pre-ozonation is being adopted in more and more waterworks (von Gunten 2003; McCurry *et al.* 2015), while there is a great probability that NDMA forms by ozone directly or during disinfection processes. However, few reports have systematically demonstrated its effect on NDMA formation in different water resources. In this paper, the formation of NDMA from four selected water sources treated with ozone or chloramine alone or with combined ozone/chloramine were investigated. Meanwhile, water-quality parameters (such as dissolved organic carbon (DOC), dissolved organic nitrogen (DON), hydrophobic fractions (HFs), positive-charged fractions (PCFs), ultraviolet absorbance at 254 nm wavelength (UV_{254}), ammonia) were determined. Moreover, the main components that affected NDMA formation were analyzed by principal component analysis.

MATERIALS AND METHODS

Water sample collection

Water samples were collected from four water-supply sources in Fujian Province of China, covering two reservoirs (#1, #2), one lake (#3) and one river (#4). All the water samples were stored at 4 °C and shipped to the laboratory, and sample analyses and treatment experiments were performed within 8 h after collection.

Pre-ozonation and chloramination of samples

All the samples were filtered through a 0.45 μm membrane, then, separated into three groups, each group was provided with three samples for parallel analysis. The first group was oxidized by 2 mg/L O_3; the second group was disinfected by 20 mg/L monochloramine; the third group was pre-oxidized by 2 mg/L O_3 first then disinfected by 20 mg/L monochloramine.

Ozonated water was made from dry oxygen produced by an ozone generator (CF-G-3–10 g/h, Guolin, China) and it was kept in an ice bath. Proper dosage of ozonated water was added to keep the O_3 concentration at 2 mg/L and then reacted for 1 h. Chloramination experiments were performed at pH 7.0 ± 0.2 (phosphate buffer solution) in 1 L brown borosilicate vials with screw caps. To evaluate the NDMA formation potential (NDMAFP), sufficient monochloramine (20 mg/L) was added to provide enough disinfectant and then the water samples were stored at 25 °C for 7 d. Analyses of NDMA were then conducted after residual disinfectant was quenched with excess ascorbic acid.

Analytical methods

NDMA was analyzed using a modified solid-phase extraction (SPE)–liquid chromatography tandem mass spectrometry (LC/MS/MS) procedure developed by Liu *et al.* (2015). Analysis of the other parameters (DOC, DON, UV_{254}, ammonia) was the same as in a previous paper (Liao *et al.* 2014). The non-polar fractions and the positive-charged fractions were analyzed by the polarity rapid assessment method (PRAM) (Liao *et al.* 2015). All the details can be seen in the Supporting Information, available with the online version of this paper.

Principal component analysis (PCA) is a powerful technique of extracting the main components of the multivariate factors and it can reduce the dimension of the space formed by multiple variables. The factor analysis procedure in IBM SPSS software (version 24) was used to develop the PCA method. Varimax with Kaiser normalization was chosen to be the rotation method.

RESULTS AND DISCUSSION

NDMA

NDMA can be formed by ozonation, and this may be a drawback for the application of ozone in drinking-water treatment (Chen *et al.* 2018). To clarify the effect of ozone directly on NDMA formation and its role in NDMA formation during the subsequent chloramination process, the amounts of NDMA were detected for the four water samples in these conditions (Figure 1).

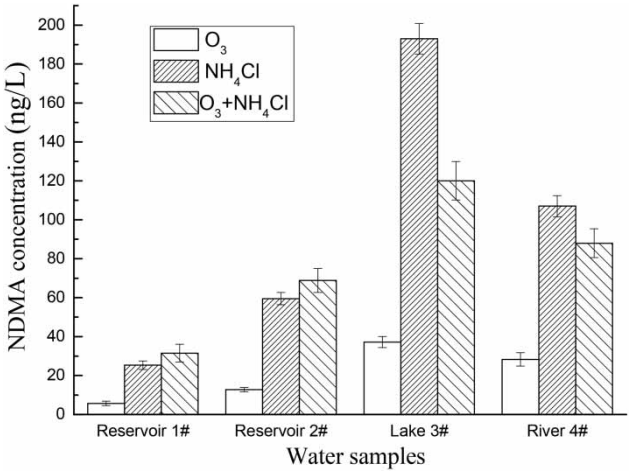

Figure 1 | NDMA formation in the four water samples.

As can be seen in Figure 1, NDMA formed directly from all the water samples no matter whether by ozonation or during chloramination. The NDMA amounts formed during chloramination (25.3–193 ng/L) were much higher than by ozonation (5.7–37.2 ng/L). That is because the chloramination reaction pathway is likely the most important one for NDMA formation in drinking-water treatment (Krasner *et al.* 2013). During both ozonation and chloramination, the concentration of NDMA in the lake water (sample #3) was much higher than in the others. The effects of pre-oxidation on subsequent chloramination differed among the selected water sources. A decrease in NDMAFP during chloramination was observed after treatment with pre-ozonation for lake water and river water, however, for reservoir water it was slightly increased.

NDMA can be formed directly during ozonation, but its amount is typically low; the result is consistent with a previous paper (Gerrity *et al.* 2015). Regarding different types of source water, the highest concentrations of NDMA were mainly found in the lake water (sample #3) no matter with what kinds of oxidation methods. The reason may be the presence of extensive discharge sources around the lake, including industrial and domestic discharges.

Although there were abundant precursors in the lake water, pre-ozonation could remove or transfer parts of them. The phenomenon was different from that of the reservoir water. That may due to the diverse properties of organic species in each specific water source; the ability of organic species to form NDMA might be different (Hao *et al.* 2017).

DON/DOC

The concentrations of DOC and DON for the four water samples were investigated and the results are illustrated in Figure 2.

The DOC of the water samples ranged from 2.56 to 4.97 mg/L, therein, DOC was particularly low in reservoir #1 (2.56 mg/L). The DOC content in the river water was the highest, while it did not form the most amount of NDMA (Figure 1), so more DOC did not mean more NDMA formation in the source water. The result was different from that of Chen *et al.* (2016), who reported that more DOC indicated elevated nitrosamine-FPs in the river water of Taiwan.

DON was the important part of soluble dissolved organic matter (DOM) in the water, and the concentrations of DON in the selected source water ranged from 0.12 to 0.45 mg/L, which accounted for 4.23–10.76% of DOC. The result was consistent with a previous paper, which reporting that the ratio of DON/DOC was in the range of 0.5–10% in water sources (Tuschall & Brezonik 1980). DON and DON/DOC ratio in the lake water were also higher than those of other samples, and so was the trend of NDMA. Hence, the formation of NDMA was probably correlated to the contamination of source water as indicated by high DON content as well as high DON/DOC ratio. This opinion was supported by Krasner, who thought that DON may correlate with NDMAFP (Krasner *et al.* 2013). However, Uzun *et al.* (2015) reported that there was only a weak correlation

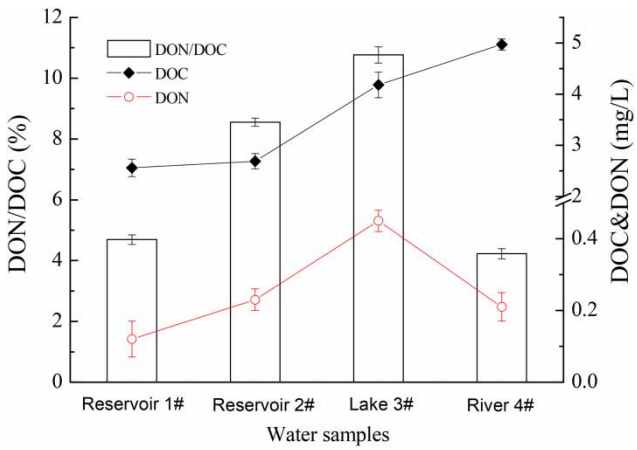

Figure 2 | DOC and DON concentrations and the ratio of DON/DOC in the four water samples.

($R^2 = 0.27$) between NDMAFP and DON. In addition, Chen & Westerhoff (2010) also reported that no direct relationships were found between mg/L levels of DON and the formation of ng/L levels of NDMA.

Hydrophobic and positive-charged fractions

The HFs and PCFs were reported to contribute to more NDMA formation during chloramination (Liao *et al.* 2015). Hence, the HF and PCF concentrations of the four water samples were analyzed, and the result can be seen in Figure 3.

The HF amounts of the four selected source waters ranged from 1.27 to 3.65 mg/L, which account for 47.2–73.4% of DOC. The maximum HF concentration was found in the river water (sample #4), while reservoir #2 had the highest HFs/DOC ratio. Neither the HF concentration nor the ratio of HFs/DOC was in line with the NDMA trend, indicating hydrophobic fractions may not play an important role on NDMA formation. Chen & Valentine (2007) thought that hydrophilic fractions tended to form more NDMA than hydrophobic acid fractions. The result was opposed to our previous study, which found that over 60% of NDMA was formed from hydrophobic fractions in a lake of southeast China (Liao *et al.* 2015). The reason may be due to the distinct natural organic matter (NOM) fractions in different water sample locations.

The maximum PCF concentration was found in the lake water (sample #3, 2.63 mg/L), which was consistent with the trend of NDMA, indicating that PCFs may be important NDMA precursors (Figure 1). It agrees with the result of our previous study (Liao *et al.* 2015). Chen *et al.* (2014) also thought that NDMA precursors had positively charged amine group, as chloramine was reported to react with the un-protonated form of the amines (Krasner *et al.* 2013), and these un-protonated amines usually have positive charges. Hence, the presence of more PCF fractions in dissolved organic matter may indicate higher NDMA formation during chloramination. Although the NDMA formation keeps pace with the PCFs, it has little to do with PCFs/DOC ratio. For example, the PCFs were the dominant fraction in reservoir #2, accounting for over 70% of the total DOC, and its NDMA formation was not the maximum.

UV_{254} and ammonia

Organic matter with ultraviolet absorbance at 254 nm wavelength (UV_{254}) conjugates C = C bonds or aromatic carbon, corresponding to primarily aromatic substances and were found to be related to NDMA formation (Chen *et al.* 2016). Ammonia was also reported to affect NDMA formation especially during chlorination (Shah & Mitch 2012). The UV_{254} and ammonia concentration of the water samples were investigated and the results are illustrated in Figure 4.

As shown in Figure 4, the values of UV_{254} ranged from 0.081 to 0.175 cm^{-1} for the selected water sources, therein, it was high up to 0.175 cm^{-1} for the river water, indicating that the river water was rich in unsaturated double bonds or aromatic organic compounds. In contrast, the lowest value of UV_{254} was found in reservoir #2. The trend of UV_{254} went against that of NDMA, implying that the

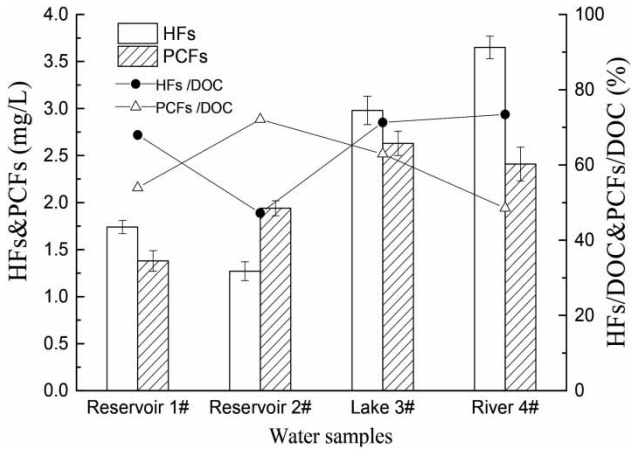

Figure 3 | Hydrophobic and positive-charged fractions in the four water samples.

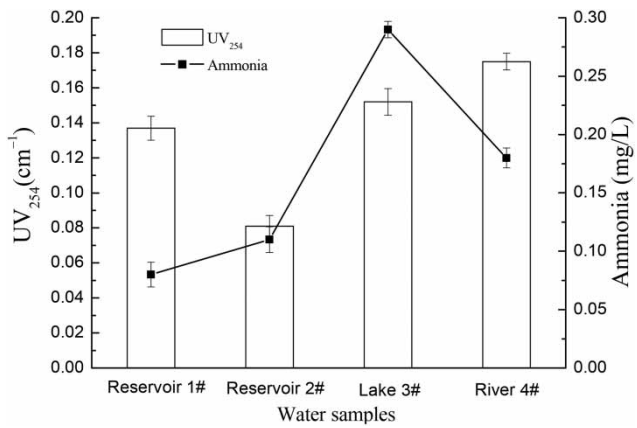

Figure 4 | UV_{254} and ammonia concentration in the four water samples.

quantities of C = C bonds or aromatic carbon compounds have a poor relationship with NDMA formation, and the R^2 of NDMA and UV_{254} was only 20.2% (Figure S1, available with the online version of this paper). This result was in accordance with the previous survey, which reported that poor correlation ($R^2 < 0.10$) was observed between NDMA and $SUVA_{254}$ (Asami *et al.* 2009). However, it was different from the study of Chen *et al.* (2016), which found that UV_{254} was extremely related to NDMA formation in a drinking-water treatment plant in Taiwan.

The highest ammonia concentration (0.29 mg/L) was detected in the lake water, and the lowest value (0.08 mg/L) was found in reservoir #1, which was also consistent with the trend of formed NDMA no matter whether by ozonation or during chloramination. The result was in accordance with the previous survey of drinking-water sources in Japan, which showed NDMA tended to be detected more frequently in samples that contained high concentrations of ammonia (Asami *et al.* 2009). However, some researchers found that a very weak correlation ($R^2 = 0.14$) was observed between the NDMA formation potential and NH_3-N during chloramination (Zhang *et al.* 2011).

Principal component analysis

PCA has been commonly applied in analyzing the factors that affect drinking water treatment (Liao *et al.* 2017). Relationships between NDMA formation and the water quality parameters have been analyzed, and the result is displayed in Figure 5.

NDMA formation is a complicated process and is influenced by many various factors, including the NOM content, various NOM fractions (DON, UV_{254}, HFs, PCFs) as well as the ammonia in the source water. All the variations in water properties are expected to play roles in NDMA formation.

Both ammonia and DON showed close relationships with NDMA formation by ozonation and during chloramination, while NDMA showed stronger correlation with ammonia by ozonation than that during chloramination. The nitrogen in ammonia plays an important role on NDMA formation for ozonation, however, during chloramination, the disinfectant can provide the other nitrogen atom for NDMA formation.

DON was found to be more related to the NDMA amounts during chloramination than those by ozonation, which may be caused by the distinct precursors for them. The compounds with structure $(CH_3)_2N$- were thought to be important NDMA precursors during chloramination disinfection, as inorganic nitrogen in chloramines can provide the other nitrogen atom in NDMA formation (Krasner *et al.* 2013), However, compounds with structure $(CH_3)_2N$-L-NH_2 have been reported to be the main precursors of NDMA during ozonation (Marti *et al.* 2015).

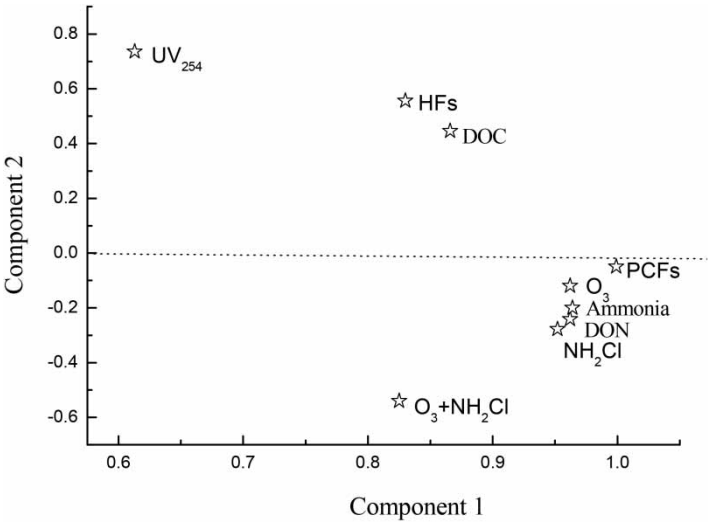

Figure 5 | The principal component analysis.

PCFs were found to be the important NDMA precursors no matter whether by ozonation or during chloramination; the result was consistent with a previous paper (Liao *et al.* 2015). HFs show a weak relationship with NDMA, and the result was similar to a previous paper, which found that hydrophilic fractions tended to form more NDMA than hydrophobic acid fractions (Chen & Valentine 2007). As shown in Figure 5, a relatively weak correlation between NDMA and UV_{254} of DOC was discovered no matter whether by ozonation, during chloramination or during the combination of ozonation/chloramination, and this result was inconsistent with a previous paper (Chen *et al.* 2016).

Overall, although an accurate relationship may not be observed due to the lower concentration (ng/L level) of NDMA compared with the relatively higher concentration (mg/L level) of water-quality parameters, the NDMA generation law may be reflected by the regular water-quality parameters. The principal component analysis demonstrated that ammonia, DON and PCFs were closely associated factors in NDMA formation in the investigated water sources, but there was no significant direct correlation between NDMA and the values of other regular water-quality parameters.

CONCLUSIONS

NDMA formation in four source waters taken from Fujian Province of China were evaluated, and the following conclusions could be drawn. NDMA can be formed directly by ozonation, however, the amounts were much lower than those formed during chloramination. Due to distinct DOM contents and fractions, the effects of ozone on NDMA formation differed in various water matrices**.** The results of principal component analysis demonstrated that ammonia, DON and PCFs of DOM have close relationships with NDMA formation and were the important NDMA precursors. Despite the advantages of implementing ozone in water treatment, the potential of forming NDMA directly or increasing NDMA formation in subsequent disinfection processes by ozonation should be noticed continuously for future drinking-water treatment systems.

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