

## Effects of natural organic matter and nitrate on the behavior of nitrosodimethylamine during ultraviolet irradiation and chloramination

Hiroshi Sakai, Tatsuro Takamatsu, Kumiko Oguma, Michio Murakami, Koji Kosaka, Mari Asami and Satoshi Takizawa

### ABSTRACT

Nitrosodimethylamine (NDMA), a potent carcinogen, is found in natural and engineered water systems. Ultraviolet (UV) treatment is potentially a useful tool for controlling NDMA at water purification plants. However, a recent study has reported that UV/advanced oxidation process (AOP) treatment may provide a source of NDMA precursors. Therefore, we investigated the effect of UV treatment on the potential for NDMA formation. Synthetic water samples containing NDMA together with Suwannee River Natural Organic Matter (SRNOM) and/or nitrate were exposed to a low-pressure (LP) UV lamp, a medium-pressure (MP) UV lamp, or a KrCl excimer lamp to determine the spectral impacts. NDMA formation potential was significantly decreased in nitrate solution by LP or MP UV exposure. Nitrate exposed to UV was assumed to have produced the OH radical, which degraded NDMA precursors. The NDMA concentration increased in solutions exposed to UV, even for those without chloramination, which contributed a certain portion of the total NDMA formation. Exposure to MP UV affected the formation of NDMA more significantly than exposure to LP UV due to the overlap of wavelengths in the MP UV emission and the absorption of nitrate.

**Key words** | 222-nm KrCl excimer UV lamp, 254-nm low-pressure UV lamp, medium-pressure UV lamp, nitrosodimethylamine, Suwannee River natural organic matter

**Hiroshi Sakai** (corresponding author)  
**Kumiko Oguma**  
**Satoshi Takizawa**  
Department of Urban Engineering,  
The University of Tokyo,  
7-3-1, Hongo,  
Bunkyo-ku,  
Tokyo 113-8656,  
Japan  
E-mail: [h\\_sakai@env.t.u-tokyo.ac.jp](mailto:h_sakai@env.t.u-tokyo.ac.jp)

**Tatsuro Takamatsu**  
Ministry of Health,  
Labour and Welfare,  
Japan

**Michio Murakami**  
'Wisdom of Water' (Suntory),  
Corporate Sponsored Research Program,  
The University of Tokyo,  
Japan

**Koji Kosaka**  
**Mari Asami**  
National Institute of Public Health,  
Japan

### INTRODUCTION

Nitrosodimethylamine (NDMA) is a potent carcinogen that is often found in natural and engineered water systems. It represents a risk level of  $10^{-6}$  at concentrations as low as 0.7 ng/L (United States Environmental Protection Agency (US EPA) 2002). The notification level in drinking water has been set at 3 ng/L in the state of California, USA (California Department of Public Health 2009), and the tentative guideline value has been set at 9 ng/L in the province of Ontario, Canada (Ministry of the Environment of Ontario 2006). Careful management of NDMA concentration is required to keep it below 10 ng/L.

NDMA can be produced chemically through the nitrosation of dimethylamine (DMA) or the oxidation of unsymmetrical dimethylhydrazine (Mitch *et al.* 2005; Shah

& Mitch 2012a). In water treatment processes, it is produced during chlorination with ammonium nitrogen, or chloramination (Choi & Valentine 2002a), as well as during ozonation processes (Asami *et al.* 2009). Formation during the sunlight photolysis of nitrite-containing water has also been reported (Lee & Yoon 2007).

Ultraviolet (UV) treatment is a promising technique that can be used to degrade NDMA. NDMA has been shown to be effectively degraded by exposure to a UV lamp (Stefan & Bolton 2002; Sharpless & Linden 2003; Zhao *et al.* 2008; Sakai *et al.* 2012) to produce dimethylamine and nitrite (Stefan & Bolton 2002). However, a previous study considering surface waters (Zhao *et al.* 2008) suggested that UV/advanced oxidation process (AOP) treatment may provide a

source of NDMA precursors. In contrast, a recent study reported that NDMA formation potential decreases as medium pressure (MP) UV irradiance increases (Shah *et al.* 2012b). To explain this controversial result, the researchers requested that further work be undertaken to determine the potential for NDMA formation during UV treatment. Negative impacts of UV treatment have been reported for other chemical compounds: chloropicrin (Reckhow *et al.* 2010), halonitromethanes and haloacetonitriles (Shah *et al.* 2011), and trihalomethanes and haloacetic acids (Bond *et al.* 2009). Therefore, we investigated potential changes in NDMA formation with a focus on water composition.

Environmental water was used in previous studies to examine the potential for NDMA formation and the impact of UV on its degradation (Zhao *et al.* 2008; Shah *et al.* 2012b), which made it difficult to attribute any differences to specific water quality parameters. Therefore, we investigated the impact of UV treatment on NDMA formation in synthetic water, enabling us to identify possible phenomena occurring during UV treatment. A synthetic water containing NDMA, Suwannee River Natural Organic Matter (SRNOM) and nitrate, was used in our experiments.

SRNOM was selected as a representative organic matter and provides a pool of NDMA precursors (Gerecke & Sedlak 2003; Chen & Valentine 2006, 2007). The UV treatment of natural organic matter could also potentially provide more NDMA precursors (Zhao *et al.* 2008). UV light absorbed into natural organic matter could initiate a variety of radical reactions (Zepp 1988). Therefore, we focused on the photochemistry of natural organic matter in relation to the potential for NDMA formation. Nitrate was expected to initiate a series of reactions including the formation of nitrite, hydroxyl (OH) radical, dinitrogen tetroxide, and peroxyxynitrous acid, following exposure to a UV lamp (Challis & Kyrtopoulos 1979; Merlet *et al.* 1985; Sharpless & Linden 2001; Vione *et al.* 2001; Sharpless *et al.* 2003; Reckhow *et al.* 2010). These reactive species may degrade NDMA precursors, while nitrite could be an agent for the nitrosation of DMA. Those possibilities were quantitatively investigated in this research.

This study examined the impact of UV treatment on the potential to form NDMA at concentrations lower than 10 ng/L. A further aim was to elucidate the roles of NOM and nitrate in NDMA formation.

## MATERIALS AND METHODS

### Outline of the experiment

Various compositions of water (original water) were prepared to examine the potential for NDMA formation and the effect of UV treatment. First, NDMA formation in the original water ( $C_O$ ) was measured following the addition of 2 mM of chloramination reagents. Second, 100 ng/L of NDMA was added into the various composition of water samples, which were then exposed to UV. The NDMA concentration after UV exposure ( $C_{UV}$ ) was measured. One set of UV-exposed water samples was used for an NDMA formation potential test by chloramination ( $C_{UVWC}$ ). The other set of UV-exposed water samples was stored under exactly the same conditions but without chloramine ( $C_{UVOC}$ ).

### UV irradiation

A monochromatic KrCl excimer lamp (UEMO20-222; USHIO, Tokyo, Japan), a monochromatic low-pressure (LP) mercury UV lamp (15 W × 2; GE/Hitachi, Tokyo, Japan), and a polychromatic medium-pressure (MP) mercury UV lamp (456 W × 1, B410MW; Ebara, Tokyo, Japan) were used. The UV irradiance of each lamp was determined by iodide/iodate actinometry (Bolton *et al.* 2011). The irradiances were 0.18 mW/cm<sup>2</sup> for the KrCl excimer lamp; 0.48 mW/cm<sup>2</sup> for the LP mercury lamp, and 1.22 mW/cm<sup>2</sup> for the MP mercury lamp. The emission spectrum of each lamp was measured using a spectrometer (USB2000; Ocean Optics, Dunedin, FL, USA).

### Water composition

Different water compositions were used to dissolve NDMA. We used Milli-Q water (Millipore, Billerica, MA), 1.5 or 3.0 mg C/L of SRNOM solution, 2.0 or 10.0 mg N/L of sodium nitrate solution, and combinations of SRNOM and nitrate (1.5 or 3.0 mg C/L of SRNOM with 2.0 or 10 mg N/L of nitrate). SRNOM was employed as one of the representative components of dissolved organic carbon (DOC) in water. The upper concentration of SRNOM and nitrate was set at the drinking water guideline value in Japan (3 mg C/L and 10 mg N/L, respectively), and the lower concentration was

an average effluent value at a water treatment plant in Tokyo (1.5 mg C/L and 2 mg N/L, respectively). SRNOM was purchased from the International Humic Substances Society (IHSS) (St Paul, MN, USA) and used as received. The detailed composition of SRNOM used in this study is shown in the supporting material (Table S1, available online at <http://www.iwaponline.com/jws/063/021.pdf>).

### NDMA formation potential test

NDMA formation potential was tested following the method proposed by Mitch & Sedlak (2002). Briefly, a 500-mL water sample was chloraminated at 2 mM and left for 10 days at 20 °C in a 0.2 M phosphate buffer (pH 7.0 ± 0.2). Chloramination was quenched by the addition of sodium thiosulfate, and samples were then provided for NDMA measurement. Monochloramine solution was prepared as in our previous report (Huy et al. 2011). Some samples were measured in duplicate or triplicate.

### NDMA measurement

Ten nanograms of NDMA d6 (Cambridge Isotope Laboratories, Andover, MA, USA) was added to 500 mL of sample solution. Water samples were provided for solid phase extraction using a Resprep cartridge (Restek, Bellefonte, PA, USA) under EPA 521 method with an extraction by dichloromethane (US EPA 2004). Water samples were analyzed by ultraperformance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS; Acquity UPLC/TQD; Waters, Milford, MA, USA) operating in electrospray/chemical positive ionization mode after a concentration to 200 µL. The NDMA concentration was corrected by the recovery ratio of NDMA d6. The detection limit of this method was 0.4 ng/L. Details of the UPLC-MS/MS analytical technique are based on our previous article (Asami et al. 2009) with minor modification.

## RESULTS AND DISCUSSION

### Degradation of NDMA by different UV lamps

NDMA was exposed to a KrCl excimer lamp, a LP UV lamp, or a MP UV lamp. Degradation of NDMA followed a

pseudo-first-order reaction. Degradation rates were 8.7, 2.7, and 2.3 cm<sup>2</sup>/J for the excimer, LP, and MP UV lamps, respectively. The degradation reaction was partly inhibited by dissolved matter in water (Table S2 in the supporting material, available online at <http://www.iwaponline.com/jws/063/021.pdf>). The average UV irradiance was calculated for an 8.82-cm-depth beaker, at 222 nm for the KrCl excimer lamp, 254 nm for the LP UV lamp, and 200–300 nm and 200–250 nm for the MP UV lamp. For monochromatic lamps, a good correlation was observed between the calculated average irradiance and the degradation rates (see Table 1 and Figure S1 (available online at <http://www.iwaponline.com/jws/063/021.pdf>)). For the MP mercury lamp, the degradation rate was correlated with UV irradiance between 200 and 300 nm ( $r^2 = 0.80$ ,  $n = 6$ ), but was more strongly correlated with UV irradiance between 200 and 250 nm ( $r^2 = 0.97$ ,  $n = 6$ ). This result suggests that UV irradiation between 200 and 250 nm is more effective at degrading NDMA than UV irradiation between 250 and 300 nm. This is plausible considering the existence of an NDMA absorption peak at 227 nm. During UV exposure, several reactions are expected to occur in parallel with NDMA degradation, such as the reduction of nitrate to nitrite and the production of NOM radicals (Zepp 1988). Despite this, a good correlation was observed between the average UV irradiance and the degradation rates. Hence, we concluded that these side reactions do not affect NDMA degradation.

### The potential for NDMA formation before UV exposure

Some of the dissolved matter has the potential for NDMA formation (Gerecke & Sedlak 2003; Chen & Valentine

**Table 1** | Determination coefficients between UV irradiance energy at a given wavelength and the degradation rate ( $n = 6$ )

	KrCl excimer ( $\lambda = 222$ )	Low- pressure mercury ( $\lambda = 254$ )	Medium- pressure mercury ( $200 < \lambda < 300$ )	Medium- pressure mercury ( $200 < \lambda < 250$ )
Determination coefficient	0.99	0.93	0.80	0.97

2007). Therefore, the potential for NDMA formation in the water samples before UV exposure was quantified.

Milli-Q water had an NDMA formation potential of  $12.5 \pm 2.0$  ng/L [ $n = 3$ , mean  $\pm$  standard error (SE)], almost the same as the previous research (Huy *et al.* 2011). NDMA in the Milli-Q water was below the detection limit (0.4 ng/L). Freshly made monochloramine solution (2 mM) was found to contain  $1.25 \pm 0.10$  ng/L ( $n = 3$ , mean  $\pm$  SE), which was almost negligible compared to the formation potential of Milli-Q water. Therefore, NDMA formation during 10 days of chloramination was assumed to be mostly attributable to the trace level of NDMA precursors in the test solution.

The NDMA formation potential was clearly increased by the addition of SRNOM in the presence of nitrate. We found that 1.5 mg C/L of SRNOM with 2.0 or 10.0 mg N/L of nitrate increased NDMA formation by 4 ng/L, and 3.0 mg C/L of SRNOM with 2.0 or 10.0 mg N/L of nitrate increased NDMA formation by 7 ng/L. The increase in NDMA formation was only 1 ng/L in 2.0 or 10.0 mg N/L of nitrate solution without SRNOM, which indicated that the presence of SRNOM played a key role in this increase. The increase in NDMA formation was proportional to the concentration of SRNOM. Note that NDMA formation was not proportional to the concentration of SRNOM without nitrate; 1.5 mg C/L of SRNOM without nitrate increased the NDMA formation potential by 5.4 ng/L, but 3.0 mg C/L of SRNOM without nitrate did not generate a proportionally large increase. A previous study recorded an NDMA formation potential of 17 ng/L with 6 mg C/L of SRNOM (Gerecke & Sedlak 2003), although the different chloramine

dose applied (1 mM) may prevent direct comparison with this study. Further investigation regarding the role of nitrate in NDMA formation is required.

### NDMA formation in UV-exposed water without chloramine

Before determining the NDMA formation potential of UV-exposed water, the NDMA concentration of UV-exposed water was measured following 10 days of storage. This experiment was conducted to determine NDMA formation during 10 days without chloramine, which represents the background formation on NDMA during the NDMA formation potential test.

NDMA concentrations are compared in Table 2. Concentrations ‘immediately after UV exposure’ and ‘10 days after UV exposure’ for each condition were treated as a paired data set in a *t*-test. In Milli-Q water, the difference was not significant for all three UV lamps. Under the other conditions, however, a significant difference was observed between concentrations ‘immediately after UV exposure’ and ‘10 days after UV exposure’ ( $p < 0.01$ ).

In water containing SRNOM, the NDMA concentration increased in all cases tested. The increments in samples exposed to LP UV were 1.9 and 3.4 ng/L for the 1.5 and 3.0 mg C/L SRNOM solutions, respectively, suggesting a linear relation between SRNOM concentration and the increase in NDMA. In samples exposed to MP UV, the increases were 5.1 and 0.9 ng/L in 1.5 and 3.0 mg C/L SRNOM solutions, respectively. Some portion of SRNOM

**Table 2** | Comparison of NDMA concentration in UV-exposed NDMA solution immediately after UV exposure ( $t = 0$ ,  $C_{UV}$ ) and 10 days after UV exposure ( $t = 10$  d,  $C_{UVOC}$ ) without chloramine addition

Solution	Low-pressure mercury (ng/L)		Medium-pressure mercury (ng/L)		KrCl excimer (ng/L)	
	$t = 0$	$t = 10$ d	$t = 0$	$t = 10$ d	$t = 0$	$t = 10$ d
Milli-Q water	1.0	0.5	0.8	0.7	2.6	1.2
1.5 mg C/L of SRNOM	1.3	3.2	5.8	10.9	3.0	–
3.0 mg C/L of SRNOM	1.0	4.4	2.0	2.9	10.7	–
2.0 mg N/L of nitrate	1.3	2.1	1.5	5.6	–	–
10.0 mg N/L of nitrate	1.5	2.2	2.0	4.8	–	–
1.5 mg C/L of SRNOM and 2.0 mg N/L of nitrate	1.3	0.9	1.9	2.9	–	–

– : not tested.



can be assumed to have been transformed to NDMA precursors during the UV exposure. In contrast to the LP exposure results, the relationship between the SRNOM concentration and the increase in NDMA was not linear for the MP exposure. Note that the UV irradiance required to achieve a similar level of NDMA degradation was substantially different for the 1.5 and 3.0 mg C/L SRNOM solutions during the MP exposure due to absorbance of the solution. It required 2,200 mJ/cm<sup>2</sup> for 1.5 mg C/L SRNOM and 4,200 mJ/cm<sup>2</sup> for 3.0 mg C/L SRNOM to degrade NDMA to a similar level. This larger irradiance likely initiated further reactions degrading the NDMA precursors.

NDMA can be produced by chloramination from SRNOM (Gerecke & Sedlak 2003; Chen & Valentine 2007), and similar reactions could have occurred during the 10 days of storage, even without chloramination. Any external energy would then be expected to promote such reactions. Following UV exposure, UV light can be absorbed into natural organic matter and can initiate a series of reactions (Zepp 1988). Then, one may speculate that UV-exposed natural organic matter could become a source of NDMA formation in terms of being both a source of energy and chemical precursors.

An increase in NDMA was also observed in the water containing nitrate. Concentrations in samples exposed to LP were 0.8 and 0.7 ng/L for the 2.0 and 10.0 mg N/L sodium nitrate solutions, respectively. In samples exposed to MP, concentrations were 4.1 and 2.8 ng/L for the 2.0 and 10.0 mg N/L sodium nitrate solutions, respectively. Nitrite is produced from nitrate following UV exposure (Mack & Bolton 1999). In addition, dimethylamine (DMA) has been reported to react with nitrite to produce NDMA (Mitch et al. 2003; Lee & Yoon 2007), and DMA and nitrite are the primary degradation products of NDMA following UV exposure (Stefan & Bolton 2002). Therefore, one can assume that DMA, as an NDMA degradation product, reacted with nitrite, as a nitrate degradation product, to reproduce NDMA. Previous research has recorded the formation of NDMA from nitrite and DMA with a yield of 0.03% (Choi & Valentine 2002b). Also, a study reported that UVA light can induce the formation of NDMA from DMA and nitrite (Lee & Yoon 2007). Therefore, NDMA reformation, at the level of a few ng/L, may occur if UV energy is transmitted to water and remains in the form of long-lived radicals.

The fact that more NDMA was measured in MP-exposed samples would support this assumption. The MP lamp emits

at a shorter wavelength than the 254 nm emitted by the LP lamp (Figure S2 in the supporting material, available online at <http://www.iwaponline.com/jws/063/021.pdf>). Such shorter wavelength radiation is more readily absorbed by nitrate, and thus a greater amount of nitrate would be converted to nitrite. When comparing the 2 mg N/L results with the 10 mg N/L results, more NDMA was clearly reformed in the 2 mg N/L solution. This might have been due to a shading effect by the nitrate because the transmittance of the solution was calculated to confirm this assumption. When compared with Milli-Q water, the transmittance of MP UV light between 200 and 250 nm was 85 and 64% for the 2.0 and 10 mg N/L solutions, respectively. This would explain the differences in NDMA measurements between the two solutions.

In a mixed solution of 1.5 mg C/L and 2.0 mg N/L, the concentration of NDMA was 0.4 and 1.0 ng/L following LP and MP UV exposure, respectively. Note that this amount does not equate to the summation of the 1.5 mg C/L result and the 2.0 mg N/L result. After UV exposure, some NDMA, SRNOM, and nitrate remained, along with UV-degradation products of NDMA, SRNOM, and nitrate. The degradation products would have been transformed to NDMA in a solution containing either SRNOM or nitrate, but this would not have occurred in a mixture of both. Identifying the phenomenon in a mixed solution would be of practical importance.

### NDMA formation potential after UV exposure

The NDMA formation potential of UV-exposed samples is shown in Table 3. Water samples originally contained SRNOM and/or nitrate with 100 ng/L of NDMA. After exposure to UV, the NDMA formation potential was measured after 10 days ( $C_{UVWC}$ ). The net increase was calculated as ( $C_{UVWC} - C_{UV}$ ) by subtracting the remaining NDMA immediately after UV exposure ( $C_{UV}$ ). These net increases after 10 days were compared with the formation potential of the original water without UV exposure as shown in Table 4 ( $C_0$ ). A significant difference was noted in the solution containing nitrate ( $p < 0.05$ ). The original formation potentials ( $C_0$ ) for 2.0 and 10 mg N/L samples were  $13.2 \pm 0.03$  ( $n = 2$ ) and  $13.3 \pm 0.4$  ( $n = 2$ ), respectively. A difference appeared between ( $C_0$ ) and ( $C_{UVWC} - C_{UV}$ ). ( $C_{UVWC} - C_{UV}$ ) decreased to  $6.70 \pm 0.66$  ( $n = 3$ ) and

**Table 3** | NDMA formation potential of UV-exposed water ( $C_{UVWC}$ ) with chloramine addition

Solution	Low-pressure mercury	Medium-pressure mercury	KrCl excimer
Milli-Q water	10.7 ± 0.9 ( $n = 3$ )	10.3 ± 0.3 ( $n = 2$ )	10.6 ± 3.1 ( $n = 2$ )
1.5 mg C/L of SRNOM	18.5 ± 0.8 ( $n = 2$ )	20.1 ± 1.5 ( $n = 3$ )	19.6 ± 0.1 ( $n = 2$ )
3.0 mg C/L of SRNOM	19.1 ± 0.8 ( $n = 3$ )	17.6 ± 1.0 ( $n = 2$ )	27.1 ± 2.1 ( $n = 2$ )
2.0 mg N/L of nitrate	8.0 ± 0.7 ( $n = 3$ )	7.8 ± 0.6 ( $n = 2$ )	–
10.0 mg N/L of nitrate	12.1 ± 0.7 ( $n = 2$ )	13.2 ± 0.6 ( $n = 2$ )	–
1.5 mg C/L of SRNOM and 2.0 mg N/L of nitrate	17.4 ± 1.5 ( $n = 2$ )	17.4 ± 1.5 ( $n = 2$ )	–

– : not tested.

**Table 4** | NDMA formation potentials in various water compositions

Water	SRNOM (mg C/L)	Sodium nitrate (mg N/L)	NDMA formation potential (ng/L) ( $C_0$ )
Milli-Q	–	–	12.5 ± 2.0 ( $n = 3$ )
Water	1.5	–	17.6 ± 0.2 ( $n = 2$ )
	3.0	–	15.6 ± 0.7 ( $n = 2$ )
	–	2.0	13.2 ± 0.03 ( $n = 2$ )
	–	10.0	13.3 ± 0.4 ( $n = 2$ )
	1.5	2.0	16.5 ± 1.7 ( $n = 2$ )
	1.5	10.0	16.2 ± 2.0 ( $n = 2$ )
	3.0	2.0	19.3 ± 0.4 ( $n = 2$ )
	3.0	10.0	19.2 ± 0.4 ( $n = 2$ )

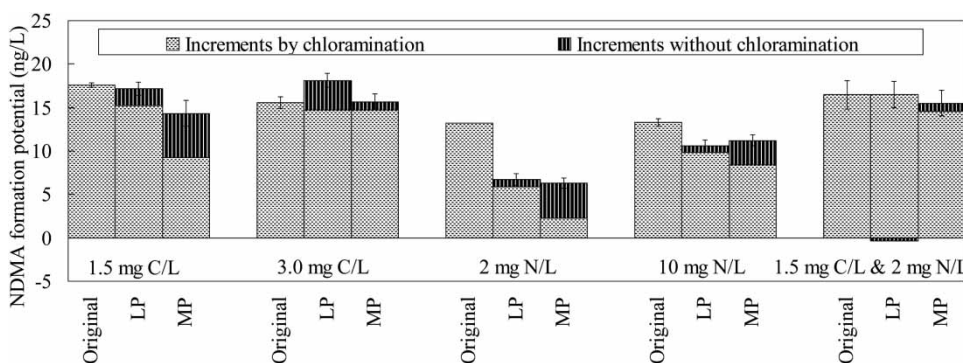
Data are shown as the mean ± standard error.

6.31 ± 0.61 ( $n = 2$ ) for the 2.0 mg N/L sample, and 10.6 ± 0.69 ( $n = 2$ ) and 11.2 ± 0.62 ( $n = 2$ ) for the 10 mg N/L sample following exposure to LP and MP UV, respectively. In the other solutions, however, no significant difference was found. In a previous research (Zhao *et al.* 2008), a significant increase was observed, which might be derived from sources other than SRNOM or nitrate.

The change in NDMA formation potential was further explored by dividing the net increase ( $C_{UVWC} - C_{UV}$ ) into increments by chloramination ( $C_{UVWC} - C_{UVOC}$ ) and without chloramination ( $C_{UVOC} - C_{UV}$ ) as shown in Figure 1.

In water containing SRNOM, NDMA formation by chloramination ( $C_{UVWC} - C_{UVOC}$ ) decreased following exposure to LP or MP UV. The decrease was 2.4 and 8.4 ng/L for the 1.5 mg C/L SRNOM solution following exposure to LP and MP UV, respectively. The decrease was 0.8 ng/L in the 3.0 mg C/L SRNOM solution following exposure to both LP and MP UV. UV exposure likely led to the degradation of SRNOM into NDMA precursors. This result agrees with one of the previous results (Shah *et al.* 2012b), possibly because nitrate concentration was low (0.6 mg N/L) and its impact was relatively small.

In nitrate solution, NDMA formation by chloramination ( $C_{UVWC} - C_{UVOC}$ ) was dramatically reduced following UV exposure. The decrease was 7.3 and 3.4 ng/L following exposure to LP UV, and 11 and 4.9 ng/L following exposure to MP UV for the 2.0 and 10 mg N/L solutions, respectively.

**Figure 1** | Comparison of NDMA formation potential between original water and UV-treated water.

This suggests that NDMA precursors in the original water were likely degraded generating a smaller NDMA formation potential in UV-exposed water. Production of the OH radical may explain this phenomenon. Nitrate can produce the OH radical following UV exposure (Sharpless & Linden 2001; Sharpless *et al.* 2003). The OH radical is an active oxygen species, which is able to oxidize various compounds in water. Therefore, OH radicals originating from nitrate can be assumed to have degraded the NDMA precursors present in the original water. The greater degradation observed in the 2.0 mg N/L solution than in the 10.0 mg N/L solution could be attributable to a larger transmittance of the solution. The greater degradation observed when using the MP lamp compared to the LP lamp could be due to the different wavelengths emitted by each lamp. While the LP lamp emits at 254 nm only, the MP lamp emits a broader wavelength (between 200 and 300 nm), which is more likely to react with nitrate.

In a mixed solution containing both 1.5 mg C/L and 2.0 mg N/L, the concentration increment by chloramination was  $15.8 \pm 0.89$  ng/L, which was similar to that of the original solution ( $16.5 \pm 1.7$  ng/L). Why this amount does not equate to the summation of the 1.5 mg C/L and 2.0 mg N/L results is difficult to explain. One possibility might be an interaction of reactive nitrogen species and NOM (Vione *et al.* 2001) increasing NDMA, as suggested in a previous review (Shah & Mitch 2012a). Further research should be undertaken to determine the exact mechanism operating in a mixed solution.

This research investigated the effects of two components, SRNOM and nitrate, on UV degradation of NDMA and formation potential of NDMA by subsequent chloramination. In those waters, formation potential was stable or decreased as in Figure 1. In contrast, an increase of formation potential was reported in a previous study (Zhao *et al.* 2008). Therefore, we need to be more careful about unknown precursors other than SRNOM and nitrate, which could increase the formation potential.

## CONCLUSIONS

The effects of SRNOM and nitrate on the formation potential of NDMA were investigated during UV-degradation experiments. Water composition affected UV degradation, which could be explained by the different UV transmittance

of the water samples. The NDMA formation potential was examined with and without chloramine. We found that NDMA formed even without chloramine during 10 days of reaction time. SRNOM and nitrate had both negative and positive effects on the NDMA formation potential. Degradation products of SRNOM may have acted as precursors of NDMA in samples without chloramination. However, SRNOM degradation contributed to a reduction in NDMA formation potential because SRNOM is an NDMA precursor. In nitrate solution, nitrate-induced nitrite and OH radicals had important roles in determining NDMA levels. Nitrite is likely to have reacted with NDMA precursors to reproduce NDMA, and the OH radical degraded NDMA precursors to reduce NDMA formation potential. Nitrate-related reactions took place more readily following exposure to the MP UV lamp than the LP UV lamp due to the larger overlap of spectra between the MP UV emission and nitrate absorption. Destruction of NDMA precursors by OH radicals dominated to reduce the 'increment by chloramine' significantly. With consideration of this phenomenon, we suggest that nitrate-induced photodecomposition should receive more attention for NDMA control. We also suggest consideration is given to the possible presence of unknown precursors which may increase NDMA formation potential.

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