Relationship between organic precursors and *N*-nitrosodimethylamine (NDMA) formation in tropical water sources

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ABSTRACT

The presence of organic compounds in water sources is one of the concerns in water treatment. They are potential precursors of disinfection byproducts (DBPs) and thus induce health problems in humans. Among the emerging DBPs, carcinogenic compound *N*-nitrosodimethylamine (NDMA) has been receiving attention during the last decade. This study examined the characteristics of organic components in various water sources and investigated their relationships with NDMA formation. Experiments were carried out on selected water samples from both natural water and wastewater. Results showed similar NDMA formation kinetics for both water sources. However, more contribution of NDMA precursors was found to be from the wastewater due to its higher organic nitrogen content. NDMA formation potential (NDMAFP) of secondary effluent ranged from 264 to 530 ng/L. A correlation study between organic compound characteristics and NDMAFP indicated that the majority of NDMA precursors came from dissolved organic nitrogen (DON) compound with small molecular weight (smaller than 500 Da), with correlation $R^2 = 0.898$. Although secondary treatment removed more than 90% of NDMA precursors, the remaining precursors in secondary effluent would still pose a challenge for water quality.

Key words | disinfection byproduct, NDMA, NDMAFP, organic characteristics, precursors

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NOMENCLATURE

ASP	Activated sludge process
BB	Building block
BP	Biopolymers
CI	Chemical ionization
DBP	Disinfection byproducts
DI	De-ionized
DMA	Dimethylamine
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
GC-MS	Gas chromatography–mass spectrometry
HOC	Hydrophobic organic carbon
HS	Humic substances
LC-MS	Liquid chromatography–mass spectrometry
LC-OCD-OND	Liquid chromatography–organic carbon detector–organic nitrogen detector
LMW	Low molecular weight
MBR	Membrane bioreactor
MDL	Method detection limit
MSD	Mass spectroscopy detector
MW	Molecular weight
NDMA	*N*-Nitrosodimethylamine
NDMAFP	*N*-Nitrosodimethylamine formation potential
NOM	Natural organic matter
SEF	Secondary effluents
SIM	Selected ion monitoring
SPE	Solid phase extraction
WRP	Water reclamation plant

INTRODUCTION

Since the beginning of the 21st century, *N*-nitrosodimethyl-amine (NDMA) has being receiving attention as one of the emerging disinfection byproducts. It is a potent carcinogen with much higher cancer potency than that of trihalo-methanes. A value of 0.7 ng/L NDMA in drinking water yields 10^{-6} lifetime cancer risk (United States Environmental Protection Agency (USEPA) 2001). NDMA has been detected in the atmosphere as well as in food and beverage production. It was first documented as a drinking water contaminant in 1998 in California. The drinking water well concerned was closed due to the detection of 150 ng/L NDMA (California Department of Health Services (CDHS) 2003). Other incidents occurred in drinking water production which took recharge from treated wastewater after a reverse osmosis system; NDMA detected exceeded 20 ng/L (Orange County Water District (OCWD) 2000).

A significant level of NDMA can be formed from chlorine disinfection of secondary wastewater effluent and surface water: 100 ng/L and less than 10 ng/L respectively (Najm & Trussell 2001; CDHS 2003). Among the chlorine disinfectants, chloramine forms relatively more NDMA (Mitch *et al*. 2003). Monochloramine causes NDMA formation one magnitude higher than that of hypochlorite (Mitch & Sedlak 2002). Chlorinated wastewater after advanced treatment, for instance microfiltration, reverse osmosis and UV disinfection, still contains NDMA with concentration ranging from 10 to 100 ng/L (Sedlak & Kavanaugh 2006).

Studies have been conducted to investigate NDMA precursors in source waters. Municipal wastewater contains a higher level of NDMA precursors compared with natural waters (Gerecke & Sedlak 2003). NDMA formation potential (NDMAFP) in secondary wastewater effluents was reported to be between 200 and 1,200 ng/L (Pehlivanoglu-Mantas & Sedlak 2006). A survey on the water resource recovery facilities in the United States showed NDMAFP in wastewater effluent to be between 660 and 2,000 ng/L (Wilczak *et al*. 2003; Sedlak & Kavanaugh 2006). Nguyen *et al*. (2011) found total NDMA precursors in ground water ranging from 4–84 ng/L, with a median of 10 ng/L. They also found that NDMA precursors in river water were significantly higher than those in ground water, ranging from 11 to 185 ng/L, with a median of 51 ng/L. In another study, NDMA precursors from Upper San Leandro reservoir (27 ng/L) and Lake Anza (48 ng/L) were found by Mitch *et al*. (2003). Dimethylamine (DMA) is one of the most frequently studied potential precursors. DMA can come from industrial products such as certain fungicides, pesticides, herbicides, drugs and amine-containing products (Child *et al*. 1996). Other precursors reported are dithiocarbamate and certain nitrogen-containing cationic polyelectrolytes (Weissmahr & Sedlak 2000).

Studies showed correlation of NDMAFP with organic carbon and organic nitrogen (Gerecke & Sedlak 2003; Farré *et al*. 2010). Farré *et al*. (2010) investigated NDMAFP in treated wastewater recycled for potable water production. They found a correlation between NDMAFP and hydrophobic organic carbon (HOC) with $R^2 = 0.95$. Most NDMA precursors (75%) exist in the size fraction of less than 1,000 Da. Pehlivanoglu-Mantas & Sedlak (2008) reported that dissolved organic nitrogen (DON) consisting of hydrophilic, low-molecular weight compounds contained most NDMA precursors, comparing to other fractions of DON. Previous studies revealed the importance of DON on NDMA formation and the positive correlation in natural waters (Lee *et al*. 2007; Dotson *et al*. 2007). Xu *et al*. (2011) also noted a strong correlation ($R^2 = 0.77$) between DON and NDMAFP in river water.

Given the complexity of NDMA precursors and the lack of information on the presence of NDMA and its precursors in tropical water sources, this work aimed to study the properties of NDMA organic precursors in different local water sources and to investigate their relationship with NDMAFP. In this study, the NDMA precursors in wastewater samples were investigated and the results were compared to those in surface water samples. Most studies apply fractionation to characterize natural organic matter (NOM) (Leenheer *et al*. 2007; Pehlivanoglu-Mantas & Sedlak 2008). It is well known that NDMA precursors are included in the DON pool; however, bulk DON measurement does not enable a clear and significant relationship to be observed between DON and NDMAFP. In this study, one recently developed approach, known as liquid chromatography–organic carbon detector–organic nitrogen

detector (LC-OCD-OND) was applied to separate NOM according to sizes and chemical functions. The quantification result of dissolved organic carbon (DOC) and DON in each fraction further enabled the correlation study between NDMAFP and NOM in each fraction. The results provided new information on the relationship between organic precursor properties and NDMAFP, which can be useful for NDMAFP removal and water quality control.

MATERIALS AND METHODS

Water samples collection

Samples were collected from two water sources with different NOM content: surface water and wastewater. They include the following: (1) lake water, (2) river water and (3) wastewater. Samples were collected from a freshwater lake located in the western region of Singapore that receives runoff from its urban catchment area. Samples were also collected from a river that receives water from tributaries and runoff from road and residential areas. All surface water samples were consistently taken at 0.5 m below the surface. The four types of wastewater selected were secondary effluents (SEF) A, B, C and primary effluent. All wastewater samples were taken consistently at the same locations in the treatment process. The characteristics and precedent treatment process are shown in Table 1. To ensure the consistency of results, all water samples were

collected in 1 L amber bottles, and stored in dark at 4 °C after collection until analyzed. All samples were processed within 10 hours of sampling. Two samples of each water type were tested.

NDMA formation potential study

In NDMAFP study, the established method by Mitch *et al.* (2003) was adopted. All glassware used was washed with decon 90 water, rinsed with de-ionized (DI) water and baked at 400 °C for at least 3 h prior to use. The reactions were conducted at room temperature in 1 L amber glass bottles. Reactions were controlled at pH = 6.8 by a 10 mM phosphate buffer. For each reaction, a 900 mL water sample was dosed with 100 mL 20 mM monochloramine. An excessive dose of monochloramine was used to make sure that the majority of the NDMA precursors were converted into NDMA. At the end of each stage, 200 mM sodium thiosulfate solution was applied to quench the reaction. The formation potential study lasted for 10 days at room temperature. A volume of 900 mL DI water was used as control blank, to measure the possible effects from reagents.

NDMA detection

NDMA was detected by applying solid phase extraction (SPE) followed by analytical instrument: gas chromatography–mass spectrometry (GC-MS) or liquid chromatography–mass

Table 1 │ Characteristics and NOM constitution of waters

Sample	Source	Description	DOC (mg/L)	DON (mg/L)	Hydrophobic content (%)	Hydrophilic content (%)
L	Lake	Watershed consists of residential and industrial areas	4.28	0.18	72.00	28.00
R	River	Receives runoff from road and residential sites	3.51	0.159	64.50	35.50
Prim Eff	WRP I	Primary sedimentation	54.00	0.888	37.00	63.00
SEF A	WRP II treatment I	Primary sedimentation, Trickling filter, Secondary sedimentation	6.26	0.287	39.10	60.90
SEF B	WRP I treatment I	Primary sedimentation, Activated sludge, Secondary sedimentation	6.53	0.348	32.50	67.50
SEF C	WRP I treatment II	Primary sedimentation, MBR	5.09	0.216	39.00	61.00

Standard deviations, d.o.f. (degree of freedom) as 6.

spectrometry (LC-MS). For SPE, EPA Method 521 cartridge was chosen. Chemicals and consumables used include: EPA 521 cartridge, SPE manifold, dichloromethane, methanol, DI water, N_2 gas, NDMA standard solution, NDMA-d_6 standard solution.

A Shimadzu 2010 gas chromatograph equipped with a mass spectroscopy detector (MSD) (Shimadzu Asia-Pacific, Singapore) and chemical ionization (CI) mode was used. Separation of NDMA was performed by a DB-5MS fused silica capillary column (30 m × 0.25 mm I.D. with 0.25 μm film thickness; J&W Scientific, Folsom, USA). The GC oven temperature was held at 35 °C for one minute, ramped at 15 °C/min to 150 °C, then ramped again at 30 °C/min to 250 °C. The MSD acquisition was performed in time scheduled selected ion monitoring (SIM) mode. The samples were injected into the GC-MS with an autosampler (AOC-20s). Splitless injection was carried out and the injection volume was 2 μL. The injector temperature was 200 °C. The ion trap was operated in the CI mode, with isobutane as reagent gas. Analytes were characterized with the SIM mode. Mean recovery was 87 ± 9%, optimal method detection limit (MDL) was 10.0 ng/L (standard deviations, d.o.f. as 6).

A LCMS-8030 triple quadrupole mass spectrometer (Shimadzu, Kyoto, Japan) was also used for NDMA analysis. The mass range was 10–2,000 m/z. A liquid chromatography (LC-30AD) with a Shimadzu SIL-30AC autosampler connected to a triple quadrupole mass spectrometer was used. Analyst software LabSolutions was used for data acquisition and analysis. A C18 capillary column (2.1 × 150 mm I.D., 5 μm) was used for separation. The mobile phases consisted of solvent B (2 mM ammonium acetate) and solvent A (100% methanol).

The solvent gradient was programmed to be 50% of solvent B for 3.5 min, increasing solvent B from 50 to 100% over 1 min, and returning back to 50% of solvent B over 0.01 min, followed by a 5.5 min re-equilibration prior to the next sample injection. The MS was programed to run for the first 6 min. The flow rate for the mobile phase was 0.3 μL/min. The sample injection was 20 μL. The MS was operated in multiple reaction-monitoring transition mode. Each transition was in positive-ion mode. MS/MS parameters were selected after the injection of NDMA and NDMA-d_6 standards in continuous-flow mode. Selected

ion pairs for NDMA and NDMA-d_6 were: NDMA 75.10 > 43.10, NDMA-d_6 81.20 > 46.10. The MS was operated at unit mass resolution, dwell time per ion pair was 150 msec.

Prior to each batch run, NDMA and NDMA-d_6 standard solutions of 5–200 μg/L were analyzed to establish a calibration curve. Methanol was used as blank solution to check for carryover in the column. Recovery of NDMA was indicated by the recovery rate of NDMA-d_6. NDMA concentration in the original sample was calculated by NDMA concentration measured divided by recovery rate. For NDMA, mean recovery was 88 ± 20%, optimal MDL was 11.7 ng/L. (Standard deviations, d.o.f. as 6. Optimal MDL is from six measurements. Duplicate SPE and triplicate LC/MS analyses.)

LC-OCD-OND analysis

An LC-OCD-OND instrument (DOC-LABOR, Germany) was applied for organic precursor analysis. It separates NOM into major fractions. It estimates the quantity of organic carbon in each fraction and the quantity of organic nitrogen in biopolymers (BP) and humic substances (HS) fractions. Major fractions are BP, HS, building block (BB), low molecular-weight (LMW) acids, LMW neutrals, and HOC.

The mobile phase applied was phosphate buffer prepared by mixing 1.5 g/L Na_2HPO_4 and 2.5 g/L KH_2PO_4. The acidification solution was prepared by mixing 4 mL *o*-phosphoric acid and 0.5 g potassium peroxodisulfate in 1 L of DI water. OCD and ultraviolet detector calibration was established on potassium hydrogen phthalate. OND calibration was established using potassium nitrate (Huber *et al.* 2011).

Data collection and processing were carried out by customized software (ChromCALC, DOC-LABOR, Germany). The nitrogen content in BP and HS fractions was estimated by the software. For the part in BB and LMW neutrals, manual integration was applied to estimate the nitrogen content in the LMW fraction and the total nitrogen (TN) content. The nitrogen in BB was then calculated by subtracting the nitrogen content in other fractions from the TN content:

N in building block = total N – N in
    biopolymers – N in humic substances – N in low
    molecular weight   (1)

Other measurements

Total chlorine was measured using the DPD (N, N-diethyl-p-phenylenediamine) method. A Hach DR5000 spectrophotometer and DPD Total Chlorine Reagent Powder Pillows were used. Total organic carbon (TOC) and TN were measured by TOC and TN analyzer (Shimadzu, Japan).

RESULTS AND DISCUSSION

NOM characteristics in different water samples

Table 1 shows a summary of the NOM composition of the six samples. The fractionation results showed that hydrophobic content, which usually contains both humic acids and fulvic acids, was the main component in lake and river water samples (72.00 and 64.50%). The hydrophilic fraction existed in a lower quantity (28.00 and 35.50%). In most of the cases, the hydrophobic fraction in natural water is higher than the hydrophilic fraction (Fabris *et al.* 2008). However, the hydrophobicity characteristic of the water samples depends on the characteristics of different water sources. The overwhelmingly dominant fraction of NOM in wastewater was hydrophilic (60.90–67.50%). Previous researchers also noted higher hydrophilic fractions presented in water sources contaminated by wastewater discharges (Mi & Myong 2005). The presence of high hydrophilic fractions is most likely related to the anthropogenic pollutants in wastewater (Lin & Wang 2011).

NDMA formation potential

NDMAFP for river water, lake water, SEF A, B, C and primary effluent are shown in Figure 1.

The different NDMA formation profiles were likely influenced by NOM in various water samples. The same profile of NDMA formation curve was observed in lake and river waters. The excess dosing of chloramines formed NDMA rapidly for the first 2 days. The concentrations of NDMA eventually plateaued due to the consumption of the organic precursors (Mitch *et al.* 2003). Similarly, the formation kinetics for three types of SEF followed the same trend. The NDMA concentration increased rapidly during the first 2 days of

reaction and reached a plateau afterward. However, for the primary effluent, although a rapid increase was observed as well within the first 2 days of reaction, concentration did not plateau after that. Figure 1 shows that for primary effluent there was still a trend of increase after 10 days.

The results for secondary effluent are comparable to similar studies in other countries. In a study in Australia, the NDMA formed from SEF from seven different treatment plants varied from 300 to 1,000 ng/L (Farré *et al.* 2010). The values for effluents A, B, C in our study were in the range of 300 to 600 ng/L. This corresponded to Australia's results. In another study (Mitch *et al.* 2003) in the United States, the NDMA formed from secondary effluent ranged from 660 to 2,000 ng/L. This is larger than both our experimental results and Australia's results. This higher level of NDMA formed might be due to the different degrees of industrial/commercial contribution. In Sedlak & Kavanaugh's study (2006), higher levels of NDMA formed were identified in an industrial area.

The types of NOM present in the samples may affect the formation potential pattern. It was found that samples with higher DOC and rich in hydrophilic content exhibited higher NDMAFP. The observation is consistent with the findings from Zhuo & Valentine (2006). This may be related to the higher nitrogen content in the hydrophilic fraction. The presence of secondary and tertiary amines and amine-based precursors (pharmaceuticals and personal care products) are closely related to NDMA formation (Kemper *et al.* 2010). Dotson *et al.* (2007) also reported the positive correlation between DON and NDMAFP in natural water. Samples with higher hydrophobic fractions (Lake and River) tended to have lower NDMAFP.

NDMA precursor analysis

Lake and river samples contained least NDMA precursor compared to the wastewater as their NDMAFP were the lowest. This might be due to the low DON content in these water samples (Table 1). A previous study also found DON to be an important precursor of NDMA (Lee *et al.* 2007). Lake water with higher DON may contain more nitrogen functional group compounds which are reactive in forming NDMA (Sutton & Sposito 2005). Primary effluent contained most NDMA precursor due to it having the highest DON
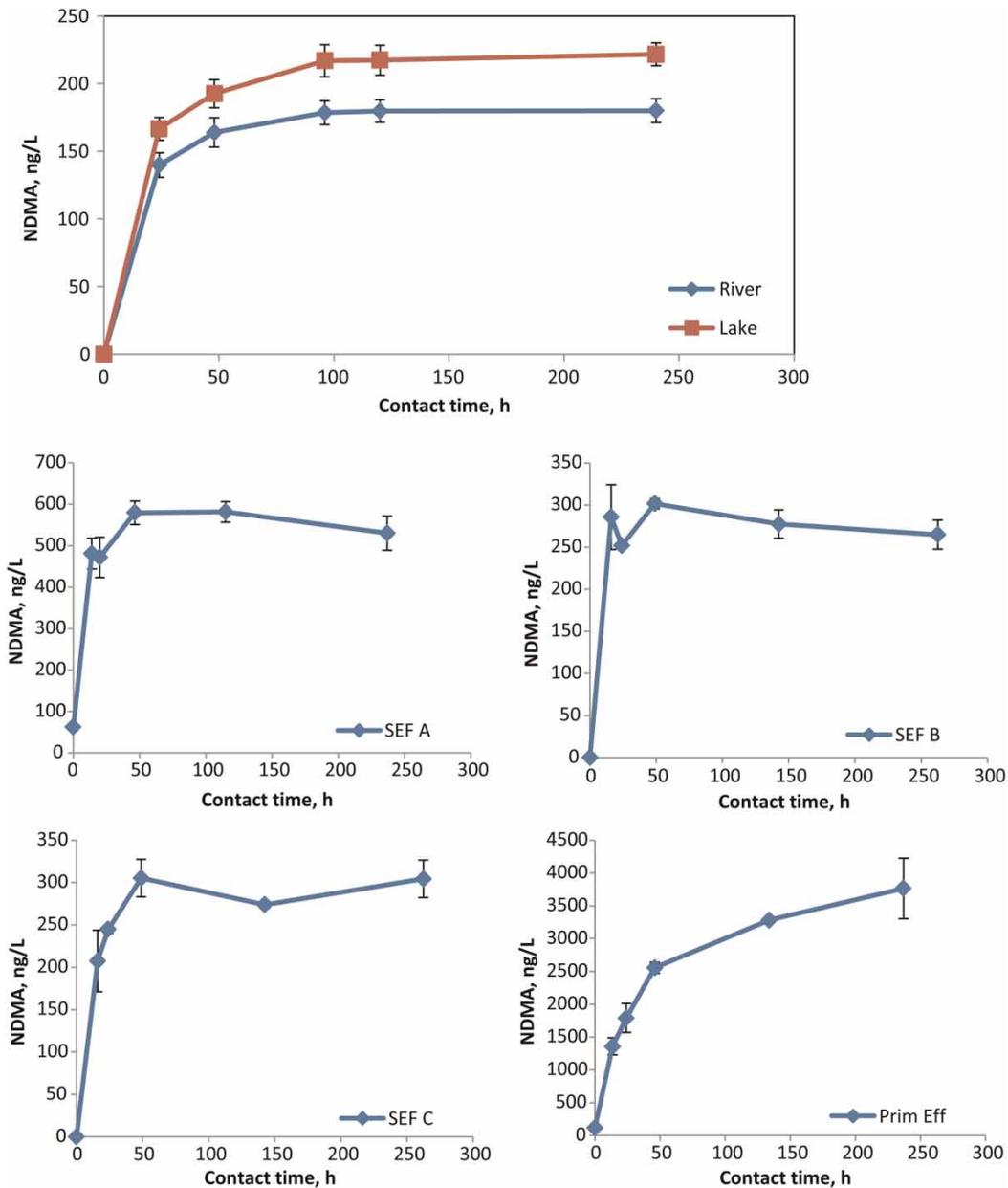
Figure 1 | NDMA formation potential for various water samples. The range bars represent one standard deviation, with d.o.f. as 6.

content. SEF had less NDMA precursor. This is probably due to the removal of DON in secondary treatment. Values of NDMAFP normalized to DOC for all samples were relatively comparable (Figure 2). However, primary effluent had an outstanding NDMAFP/DON value, more than two times that of other water samples. This might be due to the high percentage of DON associated with anthropogenic pollutants in primary effluent. These anthropogenic pollutants have more organic

nitrogen precursors to form NDMA (Gereck & Sedak 2003). Among the three SEF, SEF B had much smaller NDMAFP/DON than SEF A and C. This indicates a lower level of NDMA precursors in SEF B, which might be due to its difference organic composition which is discussed in the following sections.

Table 2 shows the DOC distribution in the water samples. The average distribution proportions of the BP in lake and
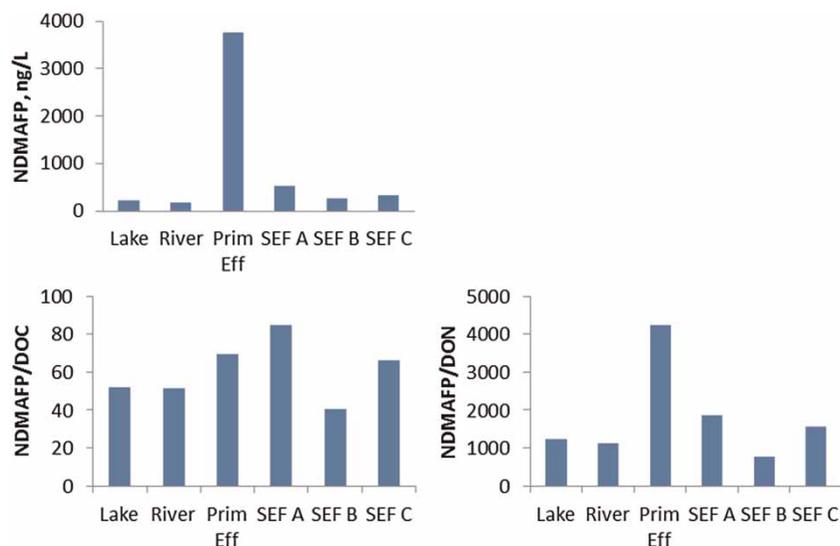
Figure 2 | NDMAFP and NDMAFP normalized to DOC and DON for various water samples.

Table 2 | DOC percentage in various water samples

	BP (%)	HS (%)	BB (%)	LMW neutrals (%)	LMW acids (%)
Lake	3.5	37.1	16.4	13.9	0.1
River	6.3	27.3	11.1	16.3	n.q.
Prim Eff	16.8	12.3	11.6	22.3	n.q.
SEF A	6.7	17.3	17.2	17.2	2.5
SEF B	9.7	19.3	18.1	18.5	1.9
SEF C	1.6	20.5	19.1	18.2	1.7

n.q. = not quantifiable (<1 ppb calculated). Standard deviations, d.o.f. as 6.

river water were 3.5% and 6.3% respectively (standard deviations, d.o.f. as 6). The relatively high percentage of HS (37.1 and 27.3%) confirmed the fractionation results which showed lake and river samples were rich in hydrophobic content. Among the wastewater samples, BP percentage in primary effluent was the highest, 16.8%; followed by moderate BP percentage in SEF A and B (6.7 and 9.7%); SEF C had the smallest BP fraction, 1.6%. This drop of BP percentage from the primary effluent to the secondary effluent was probably due to the breakdown of large organic molecules to small organic molecules. Less large organic molecules resulted in less DOC in the BP fraction. The small BP fraction of SEF C was caused by the membrane bioreactor (MBR) process which removed large molecules in the BP fraction. The relatively lower percentage of HS in wastewater (from 12.3

to 20.5%) corresponded with the results that the wastewater samples contained less hydrophobic substance. The results in this study indicated the higher NDMAFP of wastewater samples compared to that of lake and river samples. This is probably due to the higher hydrophilic fraction in wastewater samples. Zhuo & Valentine (2007) also noted that hydrophilic fractions tended to form more NDMA than hydrophobic fractions.

Table 3 shows the distribution of DON in the water samples. Results revealed that DON in the water samples accounted for more than 50% in HS and BB fractions. This indicated that HS and BB were the main components in the water samples.

Results from LC-OCD revealed that HS was the main fraction in surface water: 37.1 and 42.3% of DON in lake

Table 3 | DON percentage in various water samples

	BP (%)	HS (%)	BB (%)	LMW (%)
Lake	18.0	37.1	36.3	8.6
River	13.0	42.3	36.5	8.2
Prim Eff	17.5	40.1	34.1	8.3
SEF A	12.9	25.1	49.9	12.1
SEF B	22.7	29.9	36.4	11.0
SEF C	2.8	33.7	47.3	16.1

Standard deviations, d.o.f. as 6.

and river samples. This trend was similar to the observation for DOC content. This shows that nitrogen-containing materials from proteins and amino sugars were less significant. The organic nitrogen from the lake and river samples was largely contributed to by HS.

Among the wastewater samples, the primary effluent had the highest DON content in HS fraction and lowest DON content in low molecular weight fraction. SEF C had the lowest DON percentage in BP, indicating that the MBR was effective in removing high molecular-weight compounds.

Results showed SEF A had higher NDMAFP/DON than SEF B (Figure 2). Although SEF A and B had similar LC-OND chromatograms (Figure 3), SEF A had lower DON in BP and higher DON in BB (Table 3). Therefore DON in BB may be more correlated to NDMAFP. SEF C had higher NDMAFP/DON than SEF B. Both effluents came from the same influent wastewater; however, SEF C had lower DON in BP and higher DON in LMW fraction. Therefore, DON in LMW may also be more correlated to NDMAFP. Among the SEF, SEF B had the smallest DON content in BB and LMW (47% compared to 62% and 61% of SEF A and C, respectively). This may be the main reason for the lowest NDMAFP/DON in SEF B. These results correspond with analysis from other studies, where
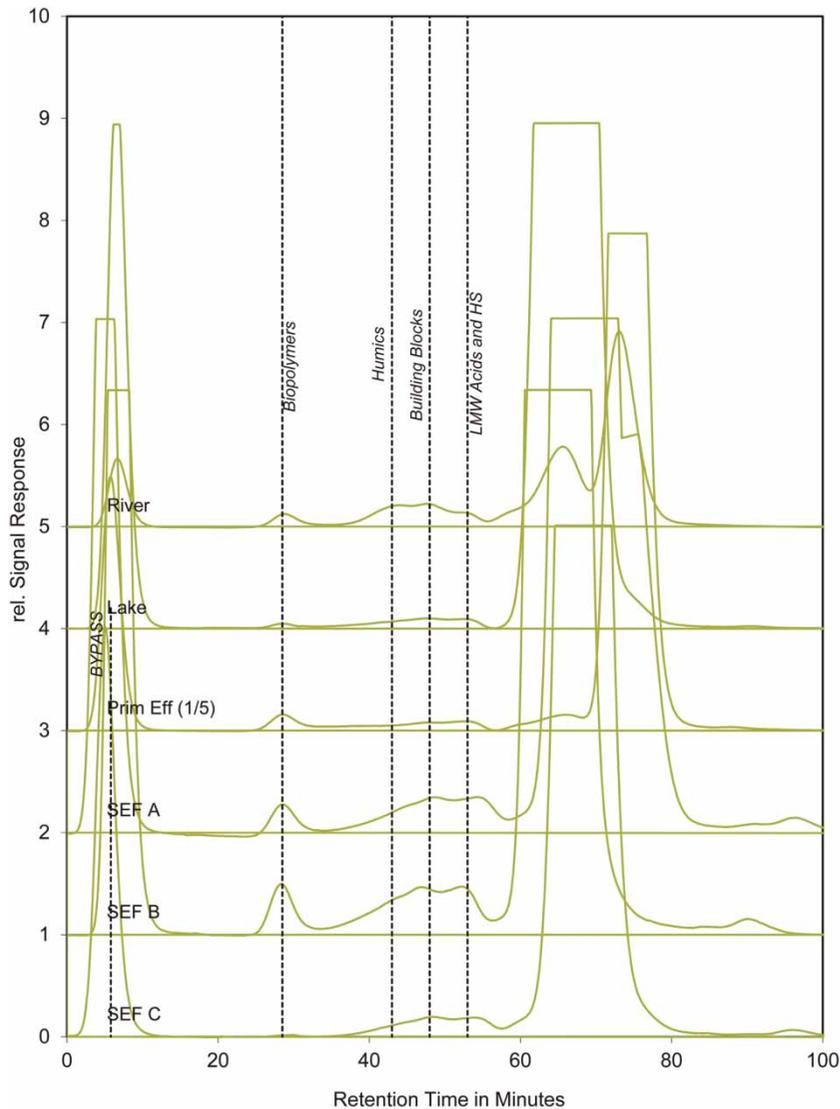

Figure 3 │ LC-OND chromatograms of various water samples.

researchers declared that molecules with MW smaller than 1,000 Da correlated to NDMAFP (Farré et al. 2010). The correlation results will be further discussed in the next section.
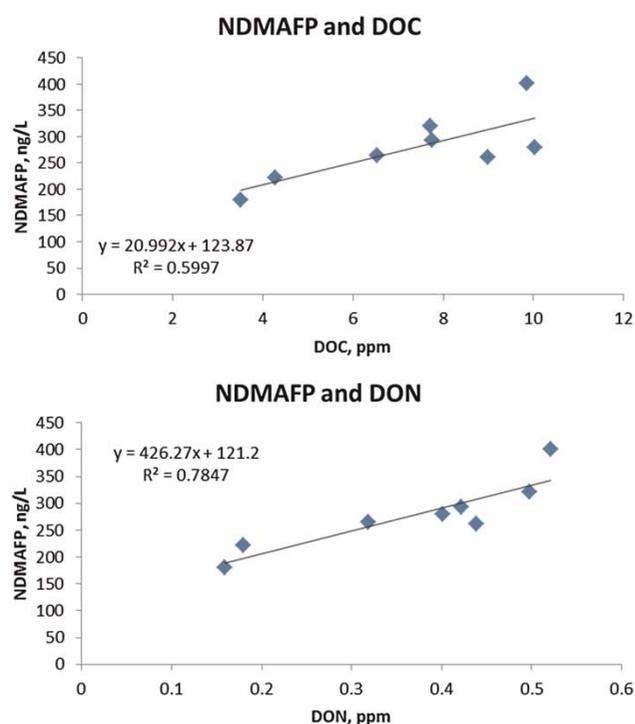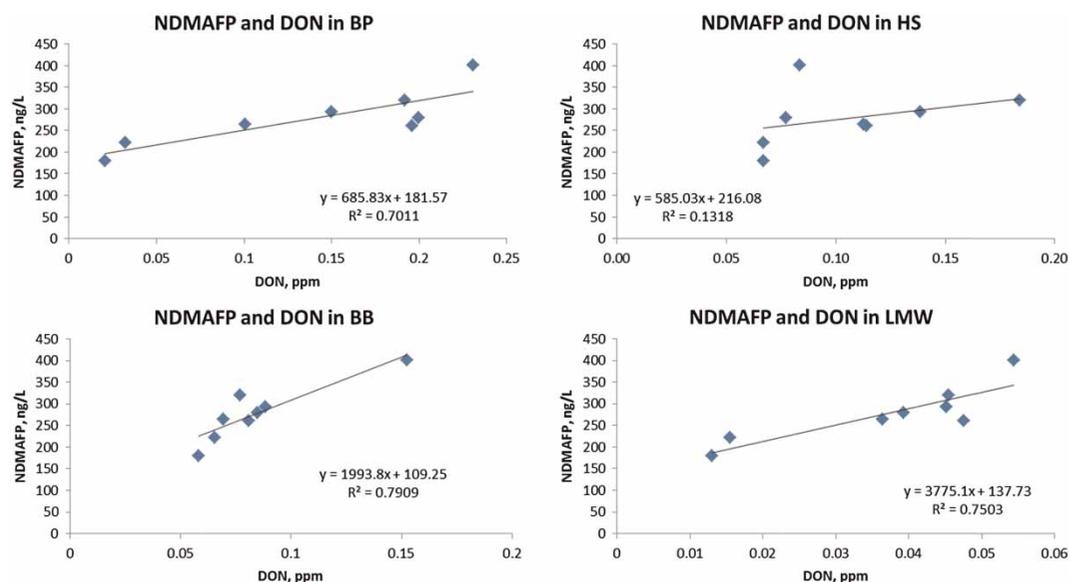

Figure 4 | Correlations between NDMAFP and DOC/DON.

Relationship between NDMAFP and organic precursors

Figures 4 and 5 show the relationship between NDMAFP and the organic precursors. A correlation study between NDMAFP and DOC indicated that the relationship was moderate ($R^2 = 0.60$), and the relationship between NDMAFP and DON was more significant ($R^2 = 0.78$). This may be because DOC is the sum of all organic carbon out of which a certain percentage is not NDMA precursors. Moreover, previous studies suggested that significant NDMA precursors are dimethylamine, tertiary or quaternary amines; these are the nitrogen containing compounds. To further investigate, correlation between NDMAFP and fractions of organic precursors was examined (Figure 5). Strong correlations were observed between NDMAFP and DON in BB ($R^2 = 0.79$) and between NDMAFP and DON in LMW ($R^2 = 0.75$). Since the molecular weight of BB is around 300 to 500 g/mol and that of LMW is less than 350 g/mol, the correlation results indicated that significant NDMA precursors came from the organic nitrogen with small molecular weight.

NDMAFP reduction in water reclamation plant (WRP)

Two types of secondary treatment, activated sludge process (ASP) and MBR, in WRP I had NDMA precursor

Figure 5 | Correlation between NDMAFP and DON in four fractions.

removal of 93% and 91%, respectively (standard deviations, d.o.f. as 6) (Figure 6). This corresponds to the reported results that NDMA precursor removal in secondary treatment was between 60 and 90% (Sedlak & Kavanaugh 2006). These high removal rates partially come from the high removal of prevalent NDMA precursor, DMA. It was reported that DMA removal in secondary treatment ranged between 96 and 99%. Studies showed that most of the remaining NDMA precursors in secondary effluent were compounds other than DMA (Mitch & Sedlak 2004; Sedlak & Kavanaugh 2006).

Table 4 indicated higher DON removal in MBR treatment; however, little difference was observed in NDMA precursor removal. This is because MBR treatment achieved more DON removal through removing large molecular weight molecules, which are less likely NDMA precursors. ASP treatment resulted in higher NDMAFP removal due to higher removal efficiency in DON associated with BB and LMW fractions (72% compared with 64% in MBR treatment).
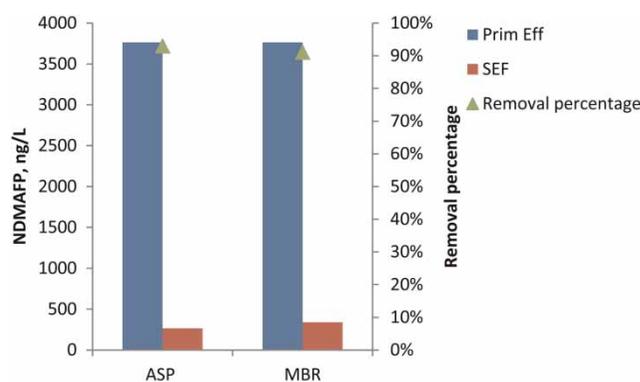

Figure 6 | NDMAFP removal by secondary treatment.

Table 4 | Comparison of NDMAFP and organics removal of two types of secondary treatment

Treatment	NDMAFP removal (%)	DOC removal (%)	DON removal (%)	DON (BB + LMW) removal (%)
ASP	93	88	61	72
MBR	91	91	76	64

Standard deviations, d.o.f. as 6.

CONCLUSIONS

The experiment results confirmed the same NDMA formation kinetics in both wastewater and natural water; however, the wastewater samples contained more NDMA precursors. NDMAFP was strongly correlated to DON ($R^2 = 0.78$), especially, DON in BB and LMW fractions. Furthermore, correlation study showed that most NDMA precursors came from the DON precursors which had low molecular weight (smaller than 500 g/mol). Secondary treatment was proved to remove a large percentage of NDMA precursors in the wastewater treatment. Future research on NDMA precursor identification and NDMA precursor removal mechanism in wastewater treatment may help improve NDMA precursor removal.

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REFERENCES

CDHS 2003 California Department of Health Services web site. http://www.dhs.ca.gov/ps/ddwem/chemicals/NDMA/history.htm (accessed 20 March 2012).

Child, P., Kaa, G., Benitz, D., Fowlie, P. & Hongyou, R. 1996 Reaction between chlorine and a dimethylamine containing polyelectrolyte leading to the formation of N-nitrosodimethylamine. In: *Proceedings of the 1996 Annual Conference of the American Water Works Association. Water Research* **100**, 23–27.

Dotson, A., Westerhoff, P. & Krasner, S. W. 2007 Nitrosamine formation from natural organic matter isolates and sunlight photolysis of nitrosamines. In *Proceedings of AWWA Annual Conference and Exposition*. Toronto, ON, Canada.

Fabris, R., Chow, C. W. K., Drikas, M. & Eikebrokk, B. 2008 Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Research* **42**, 4188–4196.

Farré, M. J., Döderer, K., Keller, J. & Gernjak, W. 2010 N-nitrosodimethylamine (NDMA) in Purified Recycled Water. http://www.urbanwateralliance.org.au/publications/UWSRA-tr34.pdf (accessed 10 May 2012).

Gerecke, A. C. & Sedlak, D. L. 2003 Precursors of N-nitrosodimethylamine (NDMA) in natural waters. *Environmental Science & Technology* **37**, 1331–1336.

Huber, S. A., Balz, A., Abert, M. & Pronk, W. 2011 Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND). *Water Research* **45** (2), 879–885.

Kemper, J. M., Walse, S. S. & Mitch, W. A. 2010 Quaternary amines as nitrosamine precursors: a role for consumer product. *Environmental Science & Technology* **44**, 1224–1231.

Lee, W., Westerhoff, P. & Croue, J. P. 2007 Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, n-nitrosodimethylamine, and trichloronitromethane. *Environmental Science & Technology* **41** (15), 5485–5490.

Leenheer, J. A., Dotson, A. & Westerhoff, P. 2007 Dissolved organic nitrogen fractionation. *Annals of Environmental Science* **1**, 45–56.

Lin, H. C. & Wang, G. S. 2011 Effects of UV/H$_2$O$_2$ on NOM fraction and corresponding DBPs formation. *Desalination* **270**, 221–226.

Mi, H. K. & Myong, J. Y. 2005 Characterization of NOM in the Han River and evaluation of treatability using UF-NF membrane. *Environmental Research* **97** (1), 116–123.

Mitch, W. A., Gerecke, A. C. & Sedlak, D. L. 2003 A N-nitrosodimethylamine (NDMA) precursor analysis for chlorination of water and wastewater. *Water Research* **37** (15), 3733–3741.

Mitch, W. A. & Sedlak, D. L. 2002 Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environmental Science & Technology* **36** (4), 588–595.

Mitch, W. A. & Sedlak, D. L. 2004 Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. *Environmental Science & Technology* **38** (5), 1445–1454.

Najm, I. & Trussell, R. R. 2001 NDMA formation in water and wastewater. *Journal – American Water Works Association* **93** (2), 92–99.

Nguyen, V. H., Michio, M., Hiroshi, S., Kumiko, O., Koji, K., Mari, A. & Satoshi, T. 2011 Occurrence and formation potential of N-nitrosodimethylamine in ground water and river water in Tokyo. *Water Research* **45**, 3369–3377.

OCWD 2000 Orange County Water District takes a proactive stance on newly regulated compound N-nitrosodimethylamine: OCWD recommends taking two drinking wells out of service. *Press release from Orange County Water District*.

Pehlivanoglu-Mantas, E. & Sedlak, D. L. 2006 The fate of wastewater-derived NDMA precursors in the aquatic environment. *Water Research* **40** (6), 1287–1293.

Pehlivanoglu-Mantas, E. & Sedlak, D. L. 2008 Measurement of dissolved organic nitrogen forms in wastewater effluents: Concentrations, size distribution and NDMA formation potential. *Water Research* **42**, 3890–3898.

Sedlak, D. L. & Kavanaugh, M. C. 2006 Removal and destruction of NDMA and NDMA precursors during wastewater treatment. WateReuse Foundation, Alexandria, VA, USA.

Sutton, R. & Sposito, G. 2005 Molecular structure in soil humic substances: the new view. *Environmental Science & Technology* **39** (23), 9009–9015.

USEPA 2001 Record of Decision for the Western Ground Water Operable Unit OU-3, Aerojet Sacramento Site. http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/cadf7f8d48234c98882574260073d787/fcc6df948bea3d488825784f0005f41b/$FILE/Aerojet_ROD_complete.pdf (accessed 22 January 2013).

Weissmahr, K. W. & Sedlak, D. L. 2000 Effect of metal complexation on the degradation of dithiocarbamate fungicides. *Environmental Toxicology Chemistry* **19**, 820–826.

Wilczak, A., Assadi-Rad, A., Lai, H. H., Hoover, L. L., Smith, J. F., Berger, R., Rodigari, F., Beland, J. W., Lazzelle, L. J., Kinicannon, E. G., Baker, H. & Heaney, C. T. 2003 Formation of NDMA in chloraminated water coagulated with DADMAC cationic polymer. *Journal – American Water Works Association* **95** (9), 94–106.

Xu, B., Ye, T., Li, D. P., Hu, C. Y., Lin, Y. L., Xia, S. J., Tian, F. X. & Gao, N. Y. 2011 Measurement of dissolved organic nitrogen in a drinking water treatment plant: size fraction, fate and relation to water quality parameters. *Science of the Total Environment* **409**, 1116–1122.

Zhuo, C. & Valentine, R. L. 2006 Modeling the formation of N-nitrosodimethylamine from the reaction of natural organic matter (NOM) with monochloramine. *Environmental Science & Technology* **40**, 7290–7297.

Zhuo, C. & Valentine, R. L. 2007 Formation of N-nitrosodimethylamine (NDMA) from humic substances in natural water. *Environmental Science & Technology* **41**, 6059–6065.