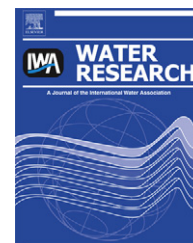


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Occurrence of nine nitrosamines and secondary amines in source water and drinking water: Potential of secondary amines as nitrosamine precursors

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ABSTRACT

Due to their high carcinogenicity, the control of nitrosamines, a group of disinfection by-products (DBPs), is an important issue for drinking water supplies. In this study, a method using ultra-performance liquid chromatography-electrospray ionization tandem mass spectrometry was improved for simultaneously analyzing nine nitrosamines in source water and finished water samples of twelve drinking water treatment plants (DWTPs) in China. The method detection limits of the nine target analytes were 0.2–0.9 ng/L for the source water samples and 0.1–0.7 ng/L for the finished water samples. Of the nine nitrosamines, six (N-nitrosodimethylamine (NDMA), nitrosodiethylamine (NDEA),

N-nitrosomorpholine (NMOR), N-nitrosodi-n-butylamine (NDBA), N-nitrosomethylethylamine (NMEA), and N-nitrosodiphenylamine (NDPhA)) were detected. The total nitrosamine concentrations in source water and finished water samples were no detection–42.4 ng/L and no detection–26.3 ng/L, respectively, and NDMA (no detection–13.9 ng/L and no detection–20.5 ng/L, respectively) and NDEA (no detection–16.3 ng/L and no detection–14.0 ng/L, respectively) were the most abundant. Meanwhile, the occurrence of nine secondary amines corresponding to the nine nitrosamines was also investigated. All of them except for di-n-propylamine were detected in some source water and finished water samples, and dimethylamine (no detection–3.9 μg/L and no detection–4.0 μg/L, respectively) and diethylamine (no detection–2.4 μg/L and no detection–1.8 μg/L, respectively) were the most abundant ones. Controlled experiments involving chloramination of four secondary amines confirmed that dimethylamine, diethylamine, morpholine and di-n-butylamine in water can form the corresponding nitrosamines, with diethylamine and morpholine showing significantly higher yields than dimethylamine which has already been identified as a precursor of NDMA. This study proved that diethylamine, morpholine and di-n-butylamine detected in raw water would be one of the important precursors of NDEA, NMOR and NDBA, respectively, in drinking water.

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1. Introduction

Nitrosamines, as a group of emerging disinfection by-products (DBPs) in drinking water particularly when chloramine is adopted as the disinfectant, have recently raised great concerns because of their high carcinogenic potency in comparison to conventional DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs). Until now, nine nitrosamines have been detected in drinking water, while N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), and N-nitrosopyrrolidine (NPyr) are the most frequently detected compounds (Asami et al., 2009; CDPH, 2007; Charrois et al., 2007; Jurado-Sanchez et al., 2010; Zhao et al., 2006). Among these nine nitrosamines, six are listed in the third Unregulated Contaminant Monitoring Regulation by the US EPA (2007), and five are in the third version of the Contaminant Candidate List (CCL3) in 2008 (EPA, 2008). The US, Canada and some other countries have established temporary regulations for NDMA, NDEA, N-nitrosodi-n-propylamine (NDPA), and N-nitrosomorpholine (NMor) at regional or even national levels (Inspectorate, 2009; OMET, 2003; Planas et al., 2008; SDWA, 2002).

To control conventional DBPs and maintain residual chlorine levels in tap water, chloramine (instead of chlorine) has been used for disinfection in some countries. In addition to direct doses of chloramine, some source waters contain relatively high concentrations of ammonia due to contamination by fertilizer and municipal wastewater (Turrentine, 1929; Wood, 2001); this leads to the formation of chloramine even when using chlorine as the disinfectant. In order to effectively control the formation of nitrosamines during water treatment, it is necessary to explore the potential precursors of these compounds. NDMA formation mechanisms during chlorination, chloramination, and ozonation processes have been extensively studied by many researchers (Chen and Young, 2008; Lorenzo et al., 2007; Oya et al., 2008; Zhao et al., 2006). It has generally been assumed that almost all precursors of NDMA contain one or more dimethylamine groups, and the NDMA formation potential is largely dependent on the structures of these precursors. Identified NDMA precursors in environmental water include dyes (such as N, N-dimethyl-p-phenylenediamine), pesticides (such as diuron), pharmaceuticals and personal care products (such as ranitidine) and rubber vulcanizing agents (such as dimethyldithiocarbamate) (Chen and Young, 2008; Fiddler et al., 1972; Vocht et al., 2007; Oya et al., 2008). Recent research has shown that some secondary amines including dimethylamine (DMA) and diphenylamine (DPhA) are also important precursors for corresponding nitrosamines (19–21). In addition to DMA and DPhA, there are other secondary amines, such as diethylamine (DEA), methylethylamine (MEA), di-n-propylamine (DPA), di-n-butylamine (DBA), morpholine (Mor), pyrrolidine (Pyr) and piperidine (Pip), that are important intermediates with significant usage in the chemical and pharmaceutical industries (Kim et al., 2009; Sacher et al., 1997). These amines can also be formed via biodegradation of proteins, amino acids, and other nitrogen-containing compounds (Brink et al., 1990; Lorenzo et al., 2007; Pietsch et al., 2001; Sacher et al., 1997). The concentrations of DMA, DEA and Mor have been

found to be no detection (ND) to 0.55, ND to 63.0, and ND to 2.5 $\mu\text{g/L}$, respectively, in surface waters in Germany (Akyuz and Ata, 2006). Pip (ND to 0.1 $\mu\text{g/L}$), Pyr (82–152 $\mu\text{g/L}$), DPhA (ND to 0.1 $\mu\text{g/L}$) and DBA (ND to 0.24 $\mu\text{g/L}$) have been detected in rivers in Turkey (Kamarei et al., 2010). These secondary amines may also serve as the precursors for corresponding nitrosamines in drinking water. However, few studies have focused on the relationship between the suspected secondary amine and corresponding nitrosamines except for DMA and DPhA (Schreiber and Mitch, 2006), although this information is necessary to better control the formation of nitrosamines in drinking water.

Several analytical methods using liquid chromatography-tandem mass spectrometry (LC-MS/MS) have been used to simultaneously determine nitrosamines in drinking water samples. However, LC-MS/MS shows relatively low sensitivity for some nitrosamines (Plumlee et al., 2008; Zhao et al., 2006). Although liquid chromatography coupled with a linear ion trap quadrupole (LTQ) Orbitrap high resolution MS (LC-MS/HRMS) has exhibited much higher sensitivities to many nitrosamines (Krauss and Hollender, 2008), an LC-MS/MS method with relatively high sensitivity is desirable for extensive environmental investigations. In this study, we improved an ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) method to simultaneously analyze the nine nitrosamines with a high sample throughput and sensitivity. Using this method, we investigated the occurrence of the nine nitrosamines, including NDMA, N-nitrosomethylethylamine (NMEA), NPyr, N-nitrosopiperidine (NPip), NMor, NDEA, NDPA, N-nitrosodi-n-butylamine (NDBA) and NDPhA in source water and finished water from twelve drinking water treatment plants (DWTPs) in China. To better characterize the potential precursors, we (1) determined nitrosamine formation potential (FP) for all of the source water samples; and (2) studied the occurrence of nine secondary amines (DMA, DPhA, DEA, MEA, DPA, DBA, Mor, Pyr and Pip) in the source water and finished water samples of the twelve DWTPs and the formation of nitrosamines through chloramination of four extensively detected amines including DMA, DEA, Mor and DBA, respectively. To the best of our knowledge, this is the first systematic study to improve the knowledge of the occurrence of secondary amine precursors and their relationships with the occurrence of corresponding nitrosamines in source water and drinking water.

2. Experimental section

2.1. Reagents

A standard solution containing 1000 $\mu\text{g/mL}$ each of NDMA, NMEA, NPyr, NPip, NMor, NDEA, NDPA, NDBA and NDPhA was purchased from Supelco (USA). [$^2\text{H}_6$] N-nitrosodimethylamine (NDMA- d_6), [$^2\text{H}_{14}$] N-nitrosodi-n-propylamine (NDPA- d_{14}) and [$^2\text{H}_6$] dimethylamine hydrochloride were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). HPLC-grade methanol, acetonitrile and hexane were purchased from Fisher Chemical Co. (USA), and dichloromethane was purchased from CNW Technologies GmbH (Germany). Resprep EPA Method 521 cartridges (6 mL/2 g) were purchased

from Restek (Milford, MA, USA), and glass fiber pads (GF/F, 0.7 μm) were obtained from Whatman International Ltd. (Maidstone, UK). PhA, MEA, DPA, DBA, Mor, Pyr and Pip were purchased from Alfa Aesar. DMA and DEA used as hydrochlorides and benzenesulfonyl chloride (>99%) were obtained from Sigma–Aldrich. Ammonium bicarbonate was purchased from Fluka (USA), and all other chemicals such as hydrochloric acid (37%) and sodium bicarbonate were obtained from Beijing Chemical Co. (China). Stock solutions for all standard substances were stored at $-20\text{ }^{\circ}\text{C}$.

2.2. Sample collection

Source water and finished water samples were collected from twelve DWTPs during November and December, 2010. Water samples were sampled in inlets and outlets of each DWTP according to the hydraulic retention time (HRT) (about 2 h). Samples were collected in amber bottles and were maintained at a temperature of $10\text{ }^{\circ}\text{C}$ during transportation to the lab. Sodium thiosulfate (20 mg/L) was added to the finished water samples to quench any chlorine residue. Information of the twelve DWTPs, include the treatment processes, water quality characteristics, and disinfection types, are shown in [Figure S4](#) and [Table S3](#). Except for DWTP 3 which adopts the advanced water treatment process (ozone-activated carbon), all of the other DWTPs adopt conventional water treatment process. Chloramine disinfection was adopted by two plants (DWTPs 1 and 12), and chlorine disinfection was adopted by the other ten plants.

2.3. Sample preparation for analyzing nitrosamines

The samples were vacuum filtered through a 0.7 μm glass fiber. After filtration, water samples (500 mL) were spiked with 20 ng/L surrogate standard (NDMA- d_6) and were basified to pH 8.0 using sodium bicarbonate. The samples were extracted using Resprep EPA 521 cartridges ([Planas et al., 2008](#)). The cartridges were preconditioned with 10 mL of hexane, followed in sequence by 20 mL of dichloromethane, 20 mL of methanol and 20 mL of ultrapure water. The samples were passed through the cartridges at a flow rate of 3–5 mL/min under vacuum conditions. The cartridges were then dried with nitrogen gas. Analytes were eluted with 15 mL of dichloromethane at a flow rate of 2–3 mL/min, 400 μL of a water/methanol solution (95:5, V/V) was added to the extracts, and the dichloromethane was completely removed using a rotary vaporator ([Krauss and Hollender, 2008](#)). Then 50 μL of 20 $\mu\text{g/L}$ surrogate standard (NDPA- d_{14}) was added and the sample volume was gravimetrically adjusted to 0.5 mL using ultrapure water. To remove possible solid particles, all samples were filtered through syringe filters (GHP Acrodisc 13 mm, 0.2 μm , PALL) prior to injection into the UPLC-MS/MS system.

2.4. UPLC-ESI-MS/MS analysis for nitrosamines

In this experiment, a Waters ACQUITY UPLC™ system (Waters, USA) consisting of an ACQUITY UPLC™ binary solvent manager and an ACQUITY UPLC™ sample manager was used. Chromatographic separation of the compounds was performed at $30\text{ }^{\circ}\text{C}$ using an ACQUITY UPLC BEH C_{18} column (150 mm \times 2.1 mm,

1.7 μm particle size) (Waters, USA). Mobile phase A was methanol, and mobile phase B was 10 mmol/L ammonium bicarbonate in ultrapure water. The following gradient was used: 0–3 min, 5% A to 45% A; 3–5 min, 45% A to 95% A; 5–7.5 min, 95% A; 7.5–8 min, 95% A to 5% A; 8.0–13.0 min, re-equilibrate with 5.0% A. The flow rate of the mobile phase was 0.2 mL/min, and the injection volume was 30 μL .

Analyses were performed using a Waters Micromass Quattro Premier XE detector equipped with an electrospray ionization source. Data acquisition was performed in the positive ion mode, and the optimized parameters were as follows: source temperature, $110\text{ }^{\circ}\text{C}$; desolvation temperature, $400\text{ }^{\circ}\text{C}$; capillary voltage, 4.0 kV; cone voltage, 28 V; desolvation gas flow, 850 L/h; cone gas flow, 50 L/h; and multiplier voltage, 650 V. Argon (99.999%) was used as the collision gas, and the argon pressure in the collision cell was maintained at 3.5e^{-3} mbar. Quantitative analysis was performed in the multiple reaction monitoring (MRM) mode. The optimal conditions for MS/MS analysis are listed in the [Supporting Information Table S1](#). All of the data were acquired and processed using MassLynx 4.1 software.

2.5. Nitrosamine formation potential test for source waters

To investigate the potential risks in drinking water, we studied the nitrosamine-FP of the twelve source water samples using a procedure employed for simulated distribution system (SDS) chlorination ([Koch et al., 1991](#)). The Cl_2 -demand (Cl_2 -D) of each sample was measured according to the APHA Standard Method prior to the experiments ([APHA, 1995](#)). For the determination of NH_2Cl -demand (NH_2Cl -D), a monochloramine solution was prepared according to a previous paper ([Yang et al., 2007](#)). The NH_2Cl -D of each sample was then measured using a method similar with that of the Cl_2 -D measurement. The samples were chlorinated and chloraminated in 500 mL amberized vials by keeping a free chlorine or chloramine residual of 1.0 mg/L after storage at $(25 \pm 1)\text{ }^{\circ}\text{C}$ for 24 h. The concentration of monochloramine was measured using the N, N-diethyl-p-phenylenediamine ferrous ammonium sulfate (DPD-FAS) method ([APHA, 1992](#)). Analyses of nitrosamines were then conducted after the residual chlorine and chloramine were quenched.

2.6. Analysis of the secondary amines in water samples

The nine secondary amines were analyzed using GC/MS after derivation with BSC according to a previously developed method ([Sacher et al., 1997](#)). Details are given in Supporting Information.

2.7. Chloramination of the secondary amines

Reaction solutions were maintained in batches of 1 L sealed amber bottles shielded from light. Unless otherwise specified, all reaction solutions were buffered with a mixture of phosphate buffer (pH 7.2). DMA, DEA, Mor or DBA were respectively added to and fully dissolved in 1 L of water solution to give a final concentration of 0.1 μM . The amine solutions were then reacted with 1.0 mM chloramines for 24 h. For a proper time

exemplified in the UPLC-MS/MS chromatograms of the detected nitrosamines in a water sample (Fig. 1(c)). NDMA, NDEA, NDBA and NMor were the most frequently detected compounds (Table S4). The total concentrations of the six detected nitrosamines in source water samples ranged from ND to 42.4 ng/L. NDMA was detected in four source water samples, with concentrations ranging from 6.4 to 13.9 ng/L, and NDEA (1.9–16.3 ng/L) and NDBA (1.0–19.9 ng/L) were detected in seven and six source water samples, respectively. NMor (1.1–2.8 ng/L), NDPhA (0.6–2.9 ng/L) and NMEA (1.0–1.2 ng/L) were detected in six, five and two samples, respectively. The concentration levels of NDMA are in the same range with those reported in previous studies (Asami et al., 2009; Charrois and Hrudey, 2007). As for the other nitrosamines, NMor was detected in raw water in Spain (2.8 ng/L), and in river water in Germany and France (92–114 ng/L) (Krauss and Hollender, 2008; Planas et al., 2008). The occurrence of these chemicals in source water indicates the presence of some discharging sources. Previous studies have shown that NDMA may be present in secondary effluents from sewage treatment systems and in effluents from industries including rubber, leather, pesticides, food processing, foundries and dyes (Chen and Young, 2008; Feng et al., 2009; Fiddler et al., 1985). NDEA, NDBA, NMor and NDPhA have been detected in emulsion products, such as condoms, baby bottle nipples, rubber, soothers and gloves, and in tobacco, meat and wines (Spatafore and Mcdemoit, 1991; Thilen and Shishoo, 2000; Verna et al., 1996). The relatively high concentrations of NDMA, NDEA and NDBA (11.9, 13.9 and 12.5 ng/L for NDMA; 16.3 and 7.9 ng/L for NDEA; 6.4 ng/L for NDBA) in source water samples from DWTPs 1, 10 and 12 were perhaps related with the contamination of source water as indicated by the relatively high ammonia concentrations (1.7, 0.38 and 0.17 mg/L, respectively).

As shown in Table S4, six nitrosamines were also detected in the finished water samples. The concentrations ranged from 4.6 to 20.5 ng/L for NDMA (found in 7/12 samples), 1.9–16.3 ng/L for NDEA (9/12), 0.4–3.4 ng/L for NDBA (6/12), 1.1–1.7 ng/L for NMor (3/12), 1.1 ng/L for NMEA (1/12) and 3.3 ng/L for NDPhA (1/12), respectively. In comparison with the previous studies, the concentrations of NDMA detected in this study are low (max. 65 ng/L in finished water in Canada and 30 ng/L in the US) (Plumlee et al., 2008), but are close to those reported in Japan (ND-2.2 ng/L in summer and ND-10 ng/L in winter) (Asami et al., 2009). As for the other nitrosamines, the concentration levels are in accordance with previously reported studies (ND-12.9 ng/L for NDEA, 1.0–7.9 ng/L for NMor, and 1.86 ± 0.13 ng/L for NDPhA) (Jurado-Sanchez et al., 2010; Planas et al., 2008; Zhao et al., 2006).

Comparing to those in source water samples, the concentrations of NDMA in finished water samples from DWTPs 1 increased by 8.6 ng/L and those from DWTPs 5, 8, 9 and 11 increased from ND to 6.7, 4.6, 8.9 and 6.2 ng/L, respectively. The concentrations of NDEA also significantly increased in the samples from DWTP 11 (from 5.2 to 14.0 ng/L) and other DWTPs (from ND to <4 ng/L). Increase of concentrations of NDBA (DWTPs 2, 3, 5 and 8) and NDPhA (DWTP 6) was also observed. In general, these results suggest that disinfection by chlorine or chloramine during drinking water treatment could produce nitrosamines due to the presence of precursors,

which are consistent with previous reports (Chen and Young, 2008; Fiddler et al., 1972; Kemper et al., 2010; Oya et al., 2008; Zhou et al., 2009). The experiment of nitrosamine-FPs of source water also supports the above observation (Table S4). The FPs of NDMA, NDEA, NMor and NDBA for both chloramination and chlorination increased prominently in many source water samples, with the highest values being 108.5, 29.9, 20.2, and 19.5 ng/L, respectively. The FPs of the four nitrosamines during chloramination were in general higher than those found during chlorination, except for DWTPs 10 and 11. In DWTP 3, the concentrations of some nitrosamines (NDMA and NDEA) in finished water samples were much lower than the FPs of source water by chloramination; this could be attributed to the removal of precursors by ozone-activated carbon treatment (ozone dose, 0.4 mg/L). The relatively high concentration of NDMA (20.5 ng/L) in finished water from DWTP 1 was perhaps attributed to chloramine disinfection.

The FPs of NDMA by chlorination in DWTPs 1, 9, 10, 11 and 12 were relatively high (30.8, 31.7, 38.5, 21.0 and 33.3 ng/L, respectively), which could be related to the formation of chloramine due to the existence of ammonia in water (1.7, 0.31, 0.38, 0.23 and 0.17 mg/L, respectively). DWTP 11 contains 0.11 mg/L nitrite, which could also contribute to the formation of NDMA (Choi and Valentine, 2003).

On the other hand, the decreases of some nitrosamines from source water to finished water samples were found in some DWTPs. The removal value of NDMA were 1.8, 4.1 and 13.9 ng/L in DWTPs 7, 12 and 10, respectively. For other nitrosamines, the removal efficiencies were 54.4–100% for NDEA (DWTPs 6, 7, 8 and 12), 39.3–100% for NMor (DWTPs 1, 6, 7 and 11), 95.5–100% for NDBA (DWTPs 1, 6, 7, 10 and 12), and 100% for NDPhA (DWTPs 1, 2, 4 and 7), respectively. Similar phenomena have also been reported in previous studies (Asami et al., 2009). Biodegradation in sand filters, or even decomposition by pre-chlorination and, chlorination during disinfection, might be responsible for the removal of nitrosamines (Eizember et al., 1979; Krauss et al., 2009). Further studies are necessary to clarify the removal mechanisms of nitrosamines.

3.3. Occurrence of the potential secondary amine precursors in source water and finished water

The occurrence of the nine secondary amines was investigated in the twelve source water and finished water samples, and the results are shown in Table S7. DMA and DEA were detected in most of the samples, with concentrations in source water samples ranging from 0.2 to 3.9 $\mu\text{g/L}$ (10/12) and 0.3–2.4 $\mu\text{g/L}$ (8/12), respectively. The other amines existed at lower concentrations and detection frequency: the concentrations of MEA, Mor, Pyr, Pip, DBA and DPhA were 0.2–1.0 (4/12), 0.1 (5/12), 0.2 (1/12), 0.3 (1/12), 0.1–0.3 (5/12) and 0.1–0.2 $\mu\text{g/L}$ (4/12), respectively, and DPA was not detected. The levels of these secondary amines in rivers are generally within the range reported in previous papers (Akyuz and Ata, 2006; Kamarei et al., 2010; Plumlee et al., 2008). The occurrence of secondary amines in source water could be due to discharges from chemical and pharmaceutical industries and municipal wastewater (Brink et al., 1990; Lorenzo et al., 2007;

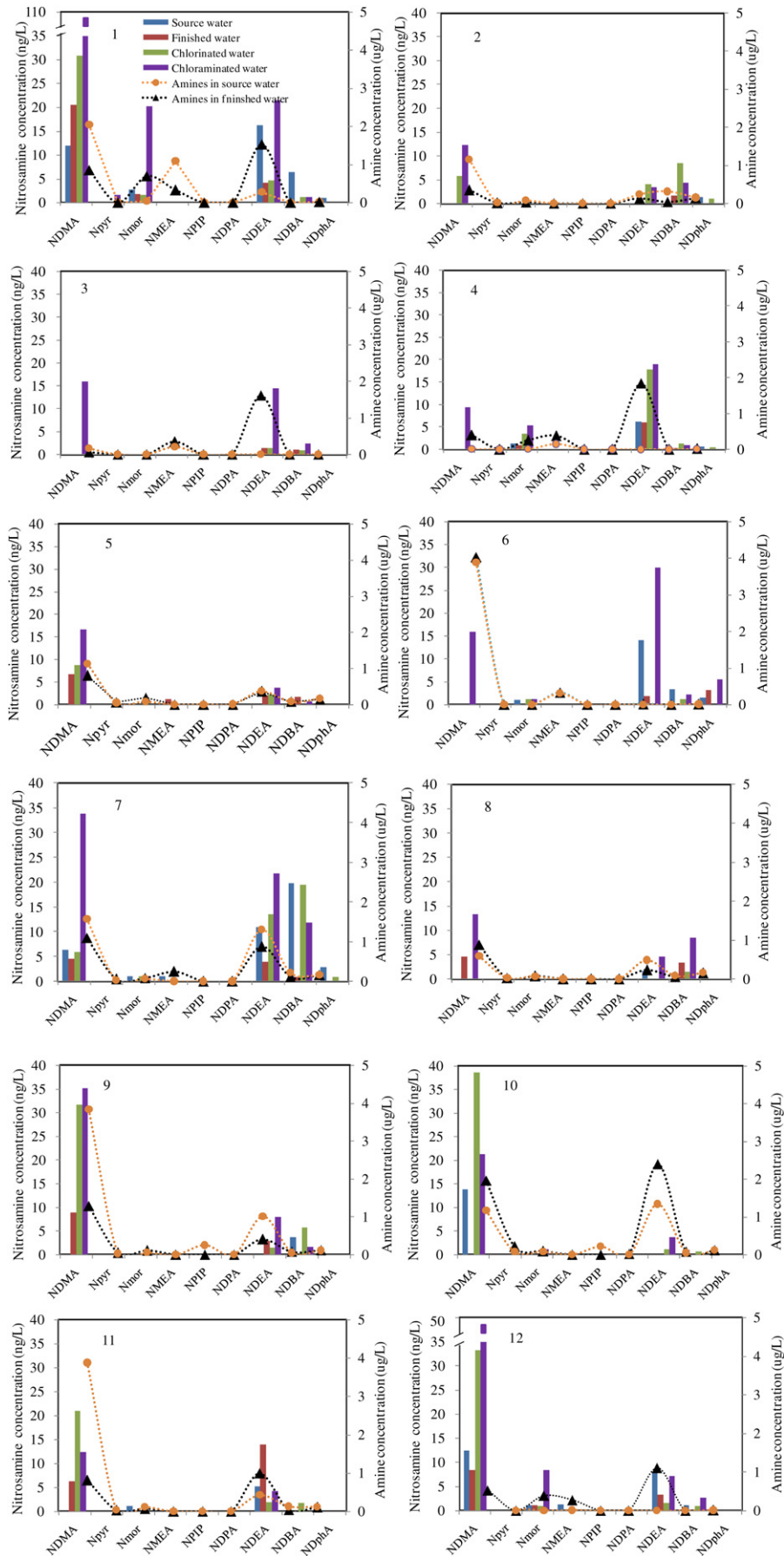


Fig. 2 – Correlations between nitrosamines and the corresponding secondary amines in water samples.

Sacher et al., 1997). Aliphatic amines like DMA, DEA, etc., are important intermediates in chemical and pharmaceutical industries, and some of them are produced in quantities of more than 100 000 tons per year in Western Europe. The concentration of DMA in an industrial waste stream, for example, was reported to be up to 100 µg/L, and that of DEA was up to 30 µg/L (Sacher et al., 1997). In this study, some source water samples (DWTPs 1, 3, 4, 5, 7, 12) were taken from inland rivers, along which a lot of industrial plants are distributed. Waste streams discharged from some of these plants may contain secondary amines.

DMA and DEA were also detected in most of the finished water samples, with concentrations ranging from 0.4 to 4.0 µg/L (11/12) and 0.1–1.8 µg/L (11/12), respectively. It is interesting that the concentrations of DMA, DEA and Mor in some finished water samples were higher than those found in source water samples. The increase of DMA concentrations was observed in samples from DWTPs 4, 8, 11 and 12 (from ND, 0.6 µg/L, 0.8 µg/L and ND to 0.4, 0.9, 3.9 and 0.5 µg/L), respectively. The increase of DEA concentrations was found in samples from DWTPs 12, 3, 4 and 1, respectively (from ND, ND, ND and 0.3 µg/L to 1.1, 1.6, 1.8 and 1.5 µg/L). These results suggest that some source water might contain C–N bond-bearing compounds that could be transformed into secondary amines during water treatment. It has been reported that some tertiary amines (e.g., trimethylamine, 3-(dimethylaminomethyl)indole, and 4-di methylaminoantipyrine) produce DMA during ClO₂ treatment (Lee et al., 2007).

Fig. 2 compares the concentrations of the secondary amines with the corresponding nitrosamines in both source water and finished water samples. In general, the presence of NDMA, NDEA, NMor and NDBA in source water, finished

water, chlorinated and chloraminated water samples was observed when the corresponding secondary amines were present, suggesting that DMA, DEA, Mor and DBA, as potential precursors, might have contributed to the formation of the nitrosamines, respectively. In addition, the detectable rates of the nine nitrosamines in finished water samples were correlated positively with the detectable rates of the corresponding secondary amines in source water samples ($r^2 = 0.87$). In fact, DMA has been identified as one of the precursors of NDMA when chloramine is used as a disinfectant (Choi and Valentine, 2002; Mitch and Sedlak, 2002). However, until now, no evidence has shown that DEA, Mor and DBA are respectively the precursors of NDEA, NMor and NDBA during disinfection. Therefore, the formation of nitrosamines from the secondary amines during chloramination was investigated in controlled experiments (Fig. 3). The results show that, in all four solutions, the concentrations of the nitrosamines increased with decreasing concentrations of the secondary amines over time, indicating that the four amines are the potential precursors of their corresponding nitrosamines.

The molar yields (Y_m) of nitrosamine formation from the four secondary amines were calculated based on Equation (1) (Zhou et al., 2009).

$$Y_m = \frac{C_{Nt}}{(C_{A0} - C_{At})} \times 100\% \quad (1)$$

where C_{A0} is the initial amine concentration (µM), and C_{Nt} (nM) and C_{At} (µM) are the concentrations of nitrosamines and amines in solution at a specified reaction time (t), respectively. The 24-h molar yield of NDEA from DEA after chloramination was the highest (5.9%), followed by Mor (4.19%), DMA (0.74%) and DBA (0.17%), and the maximum concentrations of NDMA,

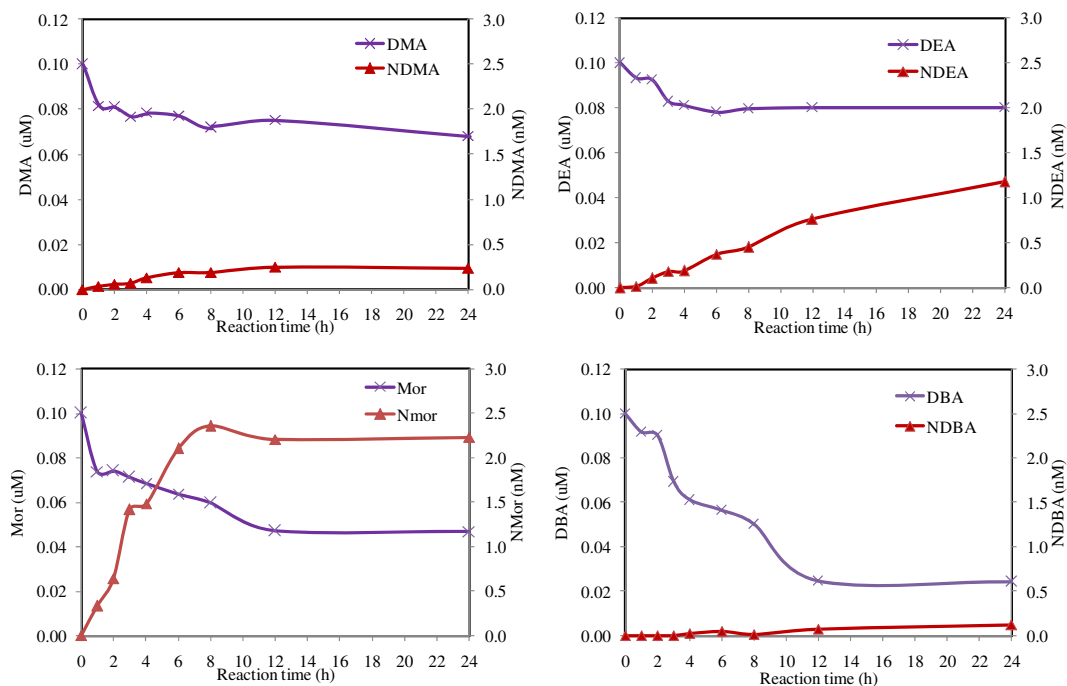


Fig. 3 – Nitrosamine formation from the secondary amines during chloramination; 0.1 µM amine (DMA, DEA, Mor and DBA) reacted with 1.0 mM chloramine, respectively.

NDEA, NMor and NDBA were 0.24, 1.18, 2.22 and 0.12 nM, respectively. The pseudo-first order reaction constants for DMA, DEA, Mor and DBA were calculated to be 0.025, 0.06, 0.31 and 0.004 h⁻¹, respectively, showing that the reactivity of different secondary amines with chloramines were quite different. Zhou et al. (2009) attributed the differences in the reactivity of secondary amines (DMA and DPhA) in forming corresponding nitrosamines (NDMA and NDPhA) to the effect of pH and structural-dependent reactivity. The pK_b values of DMA, DEA, Mor and DBA are 2.77, 3.30, 5.51 and 2.91, respectively, which might be able to explain the differences of the pseudo-first order reaction constants. The molar yield of NDMA from DMA was very low, which was in accordance with previous studies (Chen and Valentine, 2006; Mitch et al., 2003; Gerecke and Sedlak, 2003). In spite of the similar PK_b values of DBA, DMA and DEA (2.77, 3.3 and 2.91, respectively), the molar yields of their corresponding nitrosamines were quite different. There might be some other mechanisms affecting the yields of nitrosamines, which requires further study. The high yields of NDEA from DEA and NMor from Mor may explain the significant increases of corresponding nitrosamines in some finished water or chloraminated water samples (NDEA in samples from DWTPs 3, 4, 6, 7, 9 and 11 and NMor in samples from DWTPs 1 and 12). In samples from DWTPs 3 and 4, NDEA was detected in finished water samples or chlorinated/chloraminated water samples even though the corresponding secondary amine DEA was not detected in source water samples as shown in Table S7 and Fig. 2. From the fact that DEA was detected in finished water samples, it is speculated that DEA produced from some complicated C–N bond-bearing compounds was further transformed into NDEA during disinfection.

Thus, we found that nitrosamines, particularly NDMA, NDEA, NMor and NDBA are prevalent in some source water and finished water in China, and their corresponding secondary amines could be one of their precursors based on both survey and simulation results using model chemicals. The findings of this study are useful for the establishment of nitrosamine control strategies in water supply industry.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2011.06.041.

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