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Occurrence and formation potential of nitrosamines in river water and ground water along the Songhua River, China

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ABSTRACT

The presence of mutagenic and carcinogenic nitrosamines in water is of great concern. In this study, seven nitrosamines including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPyr), N-nitrosopiperidine (NPip), N-nitrosodi-n-propylamine (NDPA), and N-nitrosodi-n-butyl-amine (NDBA) were investigated in river water and ground water samples collected from 5 representative cities (Jilin, Songyuan, Harbin, Jiamusi and Tongjiang) along the Songhua River. The total concentrations of nitrosamines in ground water were n.d. (not detected) to 60.8 ng/L, NDMA was the most frequently detected nitrosamines in ground water, followed by NDEA and NPip. Relatively high detected frequency and concentrations of NDMA were also observed in river water samples, and the total nitrosamines' concentration at midstream is always higher than that at upstream and downstream. After 24 hr chlorination, concentration of NDMA, NDBA was obviously increased but NDEA was reduced. Furthermore, UV_{254} showed a better relationship with NDMA-FP rather than dissolved organic carbon (DOC), NH_4-N, and TDN.
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Introduction

As a group of emerging disinfection byproducts (DBPs) particularly when chloramine is used as the disinfectant, nitrosamines have recently raised great concerns because of their high carcinogenic potential in comparison to conventional DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs). Nitrosamines have been reported to be present not only in disinfected water but also in meats, beers, pickles, and tobacco smoke (Luo et al., 2012; Richardson and Ternes, 2014). Seven nitrosamines including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-butylamine (NDBA), N-nitrosodipropylamine (NDPA), N-nitrosomethylethylamine (NMEA), N-nitrosopiperidine (NPip) and N-nitrosopyrrolidine (NPyr) are the most frequently detected compounds in both surface and ground water (Luo et al., 2012; Guo and Krasner, 2009; Wang et al., 2011; Ma et al., 2012; Van Huy et al., 2011; Schreiber and Mitch, 2006; Mhlongo et al., 2009; Nawrocki and Andrzejewski, 2011). Nitrosamines' occurrence in surface water and ground water has been extensively investigated. A survey of Tokyo ground water and river water revealed that NDMA concentrations were <0.5–5.2 ng/L in ground water and <0.5–3.4 ng/L in river water (Van Huy et al., 2011). Up to 735.7 ng/L of the total concentrations of nitrosamines was detected at the Nakdong River, Korea (Kim et al., 2013). Ma et al. (2012) investigated the occurrence of eight nitrosamines in ground water at Jialu river basin, China and found the total concentrations of nitrosamines were n.d. (not detected) - 101.1 ng/L. The International Agency for Research on Cancer has classified NDMA and NDEA as probable carcinogens to humans (Group 2A), and NMEA, NPyr, NPip, NDPA and NDBA are classified as possible

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carcinogens to humans (Group 2B) (IARC, 1978). NDMA, NDEA, NDPA, NDPhA and NPyr are on the final version of the third Drinking Water Contaminant Candidate List (CCL-3) published by the USEPA (United States Environmental Protection Agency) in 2009. The maximum admissible concentrations of NDMA, NDEA and NMEA in water are regulated at 7, 2 and 20 ng/L, respectively by USEPA, with cancer risk estimation of 1×10^{-5}. WHO has set the guideline value for NDMA in drinking water at 100 ng/L. However, so far, there is no corresponding guideline value for nitrosamines in China.

The Songhua River is the third biggest river in China with a full length of about 1840 km, flows through Jilin and Heilongjiang Provinces into the Amur River, as the main tributary, before entering into Russia. The Songhua River is the major freshwater source for industry and agriculture, as well as the source of the drinking water of millions of residents living along it. The "2014 Report on the State of the Environment of China" shows that the Songhua River is slightly polluted (MEPOPRC, 2015), and the river water is impacted by the direct discharge of industrial wastewater and on-site leakage from decrepit sewer pipes. Nitrosamines can be discharged into waters since it can be directly formed from industrial processes such as rubber manufacturing, leather tanning, metal casting, and food processing (Mhlongo et al., 2009; Nawrocki and Andrzejewski, 2011). Nitrosamines can also be discharged into the aquatic environment via domestic sources as previous studies stated (Krauss et al., 2009; Chon et al., 2015). In addition, the industrial and domestic discharge of nitrosamines can result in the occurrence of nitrosamines in ground water (Zhou et al., 2009). Since there is no study investigating the nitrosamine occurrence at Songhua River up to our knowledge, this study is aimed to provide information about the nitrosamine contamination in surface water and ground water along the Songhua River.

1. Materials and methods

1.1. Regents

A standard solution containing 2000 μg/mL each of NDMA, NPyr, NMEA, NPip, NDPA, NDEA, and NDBA was purchased from Supelco, USA. NDMA-d_6 and NDBA-d_{14} with a concentration of 1000 μg/mL were obtained from AccuStandard, USA. HPLC (high performance liquid chromatography) grade dichloromethane, methanol, acetonitrile and acetone were purchased from Aladdin Industrial Inc., China. Activated coconut charcoal with a diameter of 100 mesh for solid phase extraction was obtained from Sigma Aldrich, USA.

1.2. Sampling information

As shown in Fig. 1, 17 river water and 24 ground water samples were collected from 5 representative cities (Jilin, Songyuan, Harbin, Jiamusi and Tongjiang) along the Songhua River during September and November 2014. The details regarding the sampling sites are provided in Table 3. Samples were collected in amber bottles and were maintained at a cool condition during transportation to the lab and stored in dark at 4°C before extraction.

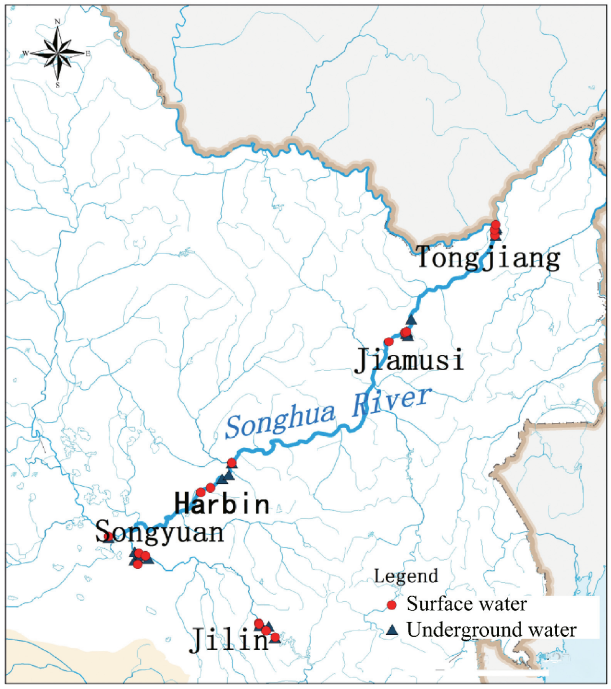

Fig. 1 – Map of sampling sites along the Songhua River.

1.3. Extraction of water samples

The samples were vacuum filtered through a 0.8 μm glass fiber before extraction. After filtration, water samples (500 mL) were spiked with 20 ng/L surrogate standard (NDMA-d6) and were adjusted to pH 8.0 using 1 g of sodium bicarbonate. The extraction of nitrosamines from the water samples was performed by solid phase extraction (SPE). Briefly, the 6 mL SPE cartridge (Supelclean™ Coconut Charcoal SPE Tube) was packed with 2.0 g activated coconut charcoal, a vacuum pump (~30 Kpa) was used to draw the water sample through the cartridge. Each packed SPE cartridge was initially rinsed with 5 mL of acetonitrile (twice) and 5 mL of methanol (twice) to remove the residual organic solvents. The SPE cartridges were then conditioned with 5 mL of methanol (twice) and 10 mL of Milli-Q water (twice). The samples passed through the SPE cartridge at a flow rate of 3–5 mL/min. The analytes absorbed on the SPE cartridge were eluted using 5 mL of dichloromethane, 5 mL of acetonitrile and 5 mL of acetone. The organic eluent was collected and concentrated down to 0.5 mL under a high purity nitrogen stream in a 40°C water bath and added Milli-Q water to 1 mL and re-concentrated to 0.5 mL, then 10 μL of 200 mg/L surrogate standard (NDPA-d_{14}) was added and the sample volume was adjusted to 1.0 mL using Milli-Q water. The extracts were stored at 4°C and analyzed using LC–MS/MS (liquid chromatography-tandem mass spectrometry) within a week.

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

In this study, a Waters ACQUITY UPLC system (Waters, USA) consisting of an ACQUITY UPLC BEH C18 column (100 mm × 2.1 mm, 1.7 μm particle size) (Waters, USA) was used for

Table 1 – Main mass fragments of seven nitrosamine compounds.

Compound	Precursor ion	Product ion	Cone voltage	Collision energy
NDMA	75.1	43.07[a]/58.00	27	11/12
NMEA	89.18	43.0/60.93[a]	23	10
NPyr	101.11	41.2/54.98[a]	26	20/13
NDEA	103.1	47/56.92[a]	29	6/10
NPip	115.1	41.03/68.92[a]	30	16/11
NDPA	131.1	43.11/88.9[a]	22	13/10
NDBA	159.15	56.98[a]/102.84	21	14/10

NDMA: N-nitrosodimethylamine; NMEA: N-nitrosomethylethylamine; NPyr: N-nitrosopyrrolidine; NDEA: N-nitrosodiethylamine; NPip: N-nitrosopiperidine; NDPA: N-nitrosodi-n-propylamine; NDBA: N-nitrosodi-n-butyl-amine.
[a] The quantitative daughter ion.

nitrosamine separation. The mobile phase was composed of methanol (eluent A) and 0.2% formic acid (eluent B). The following gradient was used: 0–2 min, 5% A; 2–6 min, 5% A to 90% A; 6–9 min, 90% A; 9–12 min, re-equilibrate with 5% A. The flow rate of the mobile phase was 0.25 mL/min for all stages and the sample injection volume was 10 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, 120°C; desolvation temperature, 380°C; capillary voltage, 3.2 KV; desolvation gas flow, 700 L/h; cone gas flow, 80 L/hr. Argon (99.999%) was used as the collision gas. Quantitative analysis was performed in the multiple reaction monitoring (MRM) mode. The optimal conditions for MS/MS analysis are listed in the Table 1. All of the data were acquired and processed using MassLynx 4.1 software.

The overall method recoveries for the target analytes were between 51.3% and 104.2%, with a relative standard deviation (RSD) less than 17.7%. The limits of quantification (LOQ) of the target analytes were between 0.5 and 10 ng/L in river and ground water (detailed in Table 2).

Table 2 – Recoveries and limits of quantification of the target compounds.

Compound	Recovery ± SD (%)	LOQ (ng/L)
NDMA	104.2 ± 17.7	2
NMEA	65.3 ± 11.2	1
NPyr	71.6 ± 7.4	10
NDEA	65 ± 2.0	1
NPip	78.2 ± 8.0	2
NDPA	58.7 ± 13.0	1
NDBA	51.3 ± 1.6	0.5

NDMA: N-nitrosodimethylamine; NMEA: N-nitrosomethylethylamine; NPyr: N-nitrosopyrrolidine; NDEA: N-nitrosodiethylamine; NPip: N-nitrosopiperidine; NDPA: N-nitrosodi-n-propylamine; SD: standard deviation; LOQ: limits of quantification; NDBA: N-nitrosodi-n-butyl-amine.

1.5. Potential for nitrosamine formation by chlorination

Nitrosamine formation potential was analyzed by following the method for the investigation of disinfection byproducts. Briefly, 500 mL water was buffered with 30 mL 0.2 mol/L monopotassium phosphate at pH 7.0 ± 0.2, chlorinated by free chlorine, and then incubated at 20°C in the dark for 24 hr. The residual free chlorine was kept at 1–2 mg Cl_2/L. Chlorine was analyzed by DPD (N, N-diethyl-p-phenylelenediamine) method at 515 nm via T6 spectrophotometer (Pgeneral, China). The reactions were halted by the addition of sodium thiosulfate solution.

1.6. Other chemical analysis

After the samples were filtered through 0.8 μm glass fiber, dissolved organic carbon (DOC), NO_2^-, NO_3^-, NH_4^+, total nitrogen (TN) and UV absorbance were analyzed. DOC and TN were analyzed with a total organic carbon analyzer (TOC-L CPH, Shimadzu, Japan). NO_2^-, NO_3^- and NH_4^+ were analyzed by ion chromatography (881 Compact IC, Metrohm, Swiss). UV absorbance at 254 nm (UV_{254}) was analyzed by a spectrophotometer (T6, Pgeneral, China).

2. Results and discussion

2.1. Overview of raw water characterization

The characteristics of raw water are presented in Table 3. The pH values ranged from 7.3 to 8.9 in 17 river water samples and from 5.9 to 7.8 in 24 ground water samples. Except sample G23, the pH of all samples are meet Chinese standards for water qualities (from 6 to 9). DOC and UV_{254} are indicators of dissolved organic compounds and humic substances, respectively. The ranges of DOC in the river water samples and ground water samples were 10.2–58.4 and 9.9–74.6 mg/L, respectively. Three river water and 14 ground water sample ammonia were higher than the regulation rule of Chinese standards for water qualities (1.0 and 0.2 mg/L for surface and ground water, respectively). The basic water parameters indicated that the water especially the ground water was polluted.

2.2. Occurrence of nitrosamines in river water

All the seven investigated nitrosamines were detected in river water samples. Nitrosamines present at various levels in all the 17 river water samples collected from five representative cities (Jilin, Songyuan, Harbin, Jiamusi and Tongjiang) along the Songhua River, northeastern China. The concentrations of the nitrosamines in river water are summarized in Fig. 2. The total concentrations of the nitrosamines in river samples ranged from 1.6 to 62.4 ng/L, with a median of 17.2 ng/L.

NDMA was obviously the most frequently (12/17 samples) detected nitrosamine and was present in the highest concentrations (0.8 to 32.0 ng/L, average: 13.4 ng/L) in river water samples, these findings are consistent with the results of previous studies in surface water and drinking water in China

Table 3 – Description of sampling sites and characteristics of raw water.

Sample site		Location		pH	DOC (mg/L)	NH_4^+ (mg/L)
River water samples	R1	126°40′42.38″ E	43°43′43.40″ N	7.3	10.2	0.37
	R2	126°33′35.39″ E	43°50′05.07″ N	7.5	10.8	0.73
	R3	126°28′30.32″ E	43°56′45.37″ N	7.4	13.1	1.02
	R4	126°28′41.80″ E	43°55′54.93″ N	7.4	29.6	0.36
	R5	124°22′15.83″ E	45°26′17.21″ N	8.9	21.6	0.36
	R6	124°48′19.09″ E	45°09′20.24″ N	8.3	12.2	1.24
	R7	124°44′30.13″ E	45°11′20.41″ N	7.6	58.4	8.96
	R8	124°54′29.44″ E	45°05′54.49″ N	7.9	24.1	0.25
	R9	126°38′54.02″ E	45°48′53.05″ N	8.0	24.4	0.31
	R10	126°26′35.15″ E	45°44′03.56″ N	7.8	16.8	0.16
	R11	126°41′46.84″ E	45°54′59.32″ N	8.7	16.6	0.30
	R12	130°16′19.65″ E	46°50′13.74″ N	7.4	13.9	0.21
	R13	130°21′21.98″ E	46°49′08.28″ N	7.3	13.8	0.35
	R14	130°23′23.58″ E	46°49′26.20″ N	7.5	14.4	0.67
	R15	132°26′36.24″ E	47°34′49.56″ N	7.4	15.1	0.17
	R16	132°28′14.22″ E	47°38′45.24″ N	7.5	13.1	0.26
	R17	132°31′13.92″ E	47°41′58.74″ N	7.6	13.5	0.28
Ground water samples	G1	126°40′27.61″ E	43°43′38.90″ N	7.0	23.6	0.35
	G2	126°39′53.97″ E	43°43′19.80″ N	7.0	35.8	2.14
	G3	126°37′11.13″ E	43°52′47.95″ N	6.9	18.7	1.81
	G4	126°29′48.82″ E	43°55′59.39″ N	7.8	10.5	1.65
	G5	126°28′33.32″ E	43°54′45.37″ N	7.0	19.4	0.81
	G6	124°21′34.52″ E	45°25′20.45″ N	7.4	60.1	1.29
	G7	124°45′34.39″ E	45°06′04.88″ N	7.1	73.6	2.50
	G8	124°42′11.62″ E	45°04′45.63″ N	7.2	74.6	0.96
	G9	124°44′23.89″ E	45°10′44.76″ N	7.2	52.3	3.65
	G10	124°49′21.18″ E	45°08′13.25″ N	7.4	59.6	2.56
	G11	124°49′57.93″ E	45°07′01.66″ N	6.9	59.8	2.77
	G12	124°56′32.85″ E	45°03′25.70″ N	7.4	63.8	0.36
	G13	126°38′14.85″ E	45°49′18.52″ N	7.1	36.0	0.78
	G14	126°28′45.02″ E	45°40′42.81″ N	7.2	60.7	0.09
	G15	126°39′41.04″ E	45°47′33.21″ N	7.2	32.6	0.85
	G16	130°15′34.31″ E	46°50′42.47″ N	6.8	18.1	0.03
	G17	130°23′34.83″ E	46°49′30.68″ N	7.4	18.5	0.05
	G18	130°23′30.22″ E	46°48′04.20″ N	6.7	26.1	0.38
	G19	130°22′27.58″ E	46°47′37.37″ N	7.1	29.9	0.62
	G20	130°23′01.88″ E	46°45′57.11″ N	7.3	62.4	0.17
	G21	130°21′32.66″ E	46°48′15.05″ N	6.6	33.3	0.03
	G22	132°27′01.08″ E	47°34′30.42″ N	6.1	9.9	0.02
	G23	132°29′24.66″ E	47°38′30.78″ N	5.9	17.7	0.03
	G24	132°30′51.72″ E	47°39′34.56″ N	6.1	22.7	0.60

DOC: dissolved organic carbon.

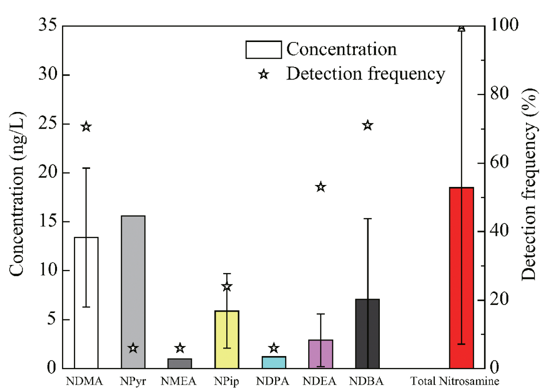

Fig. 2 – Concentrations and detection frequency of nitrosamines in river water samples.

(Wang et al., 2011; Ma et al., 2012). The concentrations of NDMA in river samples in the current study were comparable to those in Quinnipiac River in the U.S. (4 to 32 ng/L) (Schreiber and Mitch, 2006) and in Nakdong river in Korea (n.d. to 33.8 ng/L) (Kim et al., 2013), but higher than those in surface water in China (n.d. to 13.9 ng/L) (Wang et al., 2011) and Japan (n.d. to 4.3 ng/L) (Asami et al., 2009) and Tokyo (n.d. to 3.4 ng/L) (Van Huy et al., 2011), but much lower than that in Jialu River basin in China (up to 334.9 ng/L) (Ma et al., 2012).

NDBA was another most (12/17 samples) frequently detected compounds (0.8 to 32.0 ng/L, average: 7.1 ng/L), followed by NDEA (9/17 samples, 0.4 to 8.0 ng/L, average: 2.9 ng/L) and NPip (4/17 samples, 1.6 to 9.2 ng/L, average: 5.8 ng/L). NMEA and NDPA were only detected in the sample R2, with the concentration of 1.0 ng/L and 1.2 ng/L, respectively. NPyr was only detected in the sample R6 with a concentration of 15.6 ng/L.

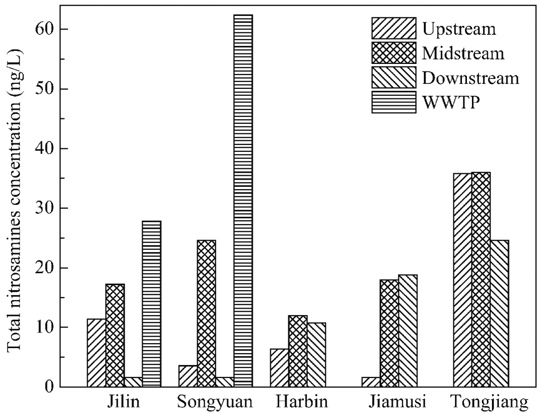

Fig. 3 – Vibration of total nitrosamines' concentration along the downstream.

Kim et al. (2013) investigated nitrosamines' concentrations at Korean surface water of Nakdong river and found that the total nitrosamines' concentration decreased exponentially along downstream. By contrast, our study generated different results. Fig. 3 shows the vibration of total nitrosamines' concentration along the downstream of each city. The total nitrosamines' concentration at midstream is always higher than that at upstream and downstream in all the five cities. This may be because the nitrosamine in river comes from the discharge of industrial and sewage wastewater which result in higher nitrosamines at midstream. Along with the downstream, contributing to the biodegradation (Zhou et al., 2009) and dilution the nitrosamines' concentration decreased. A much higher nitrosamines' concentration sample was taken from about 0.5 km downstream the waste water treatment plant (WWTP) discharge of Songyuan city. This finding can demonstrate that WWTP is a major source of nitrosamine (Nawrocki and Andrzejewski, 2011).

2.3. Occurrence of nitrosamines in ground water

Five nitrosamines including NDMA, NDBA, NDEA, NPip and NEMA were detected in 20 out of 24 ground water samples at various levels. As shown in Fig. 4, the total concentrations of the nitrosamines in ground water ranged from n.d. to

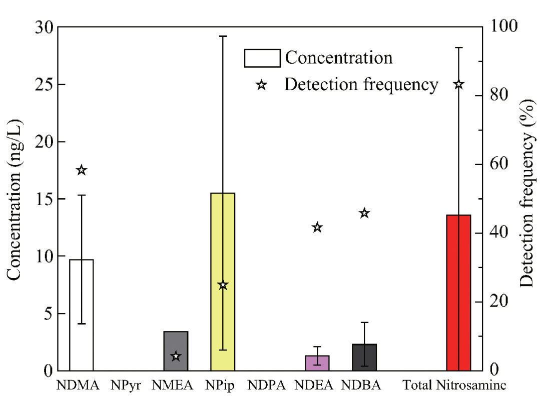

Fig. 4 – Concentrations and detection frequency of nitrosamines in ground water sample.

60.8 ng/L, with an average concentration of 13.5 ng/L. Similar to previous studies (Zhou et al., 2009; Ma et al., 2012; Van Huy et al., 2011; Mitch et al., 2003), NDMA was the most frequently detected nitrosamines (14/24 samples) in ground water samples with the concentration rang of 0.6 to 18.0 ng/L and an average concentration of 9.7 ng/L. The concentrations of NDMA in the current study were close to those in shallow ground water collected from the Jialu River basin, China (9.8 ± 12.7 ng/L) (Ma et al., 2012), and higher than those in ground water collected in Tokyo, Japan (<0.5 to 5.2 ng/L) (Van Huy et al., 2011), but lower than those in ground water affected by water reclamation plants (WRPs) in the U.S. (up to 600 ng/L) (Zhou et al., 2009). NDBA (0.2 to 6.8 ng/L, average: 2.3 ng/L), NDEA (0.6 to 2.6 ng/L, average: 1.3 ng/L) and NPip (5.2 to 41.8 ng/L, average: 15.5 ng/L) were detected in eleven, ten and six ground water samples, respectively. NMEA was only detected in sample G2 with a concentration of 3.4 ng/L. Both NPyr and NDPA were not detected from any ground sample. To our knowledge, there is little information concerning the occurrences of nitrosamines other than NDMA in ground water. The concentrations of NDBA (0.8 ± 7.2 ng/L) in ground water samples from Jialu River basin were close to our study, but NDEA concentrations were relatively higher (6.4 ± 13.0 ng/L) (Ma et al., 2012). The maximum concentration of NPip (41.8 ng/L) in ground water was about 6 times higher than those reported in drinking water treatment plants in China (n.d. to 6.9 ng/L) (Luo et al., 2012; Wang et al., 2011).

As mentioned before, the Songhua River is the major freshwater source for of the drinking water of millions of residents living along it. The widely detected nitrosamines especially NDMA would pose a cancer risk to populations using the river water and ground water as drinking water source in this area. We estimated the cancer risk (R) of NDMA according to the previous works by the following equation:

$$R = \frac{1}{10000} \times \sum_{j=1}^{j=10000} C_j \times \text{Baseline}$$

where C_j is the median or maximum concentration of NDMA that was estimated by the bootstrap method, j is the sampling time in the bootstrap method, and Baseline is the drinking water unit risk of NDMA. The unit risk of NDMA used in this study was 1.4×10^{-3} μg/L (US EPA, 2007). The estimated median and maximum cancer risks for NDMA in this study were 1.6×10^{-5} and 3.2×10^{-5}, respectively. The estimated risk is higher than the default acceptable level (10^{-5}), and close to that (1.36×10^{-5}) in the Jialu River basin (Ma et al., 2012). These results demonstrate the need for effective control of NDMA in Songhua River area.

2.4. Formation potential of nitrosamines

The results of the nitrosamine-FPs in the 17 river water and 24 ground water samples are presented in Fig. 5. The total concentrations of nitrosamine FPs ranged from 1.7 to 72.1 ng/L (average: 32.0 ng/L) and 1.1 to 37.3 ng/L (average: 13.4 ng/L) in river and ground water, respectively. NDMA, NDBA and NDEA were the three main nitrosamines of the FPs in both river and ground waters, and NDMA was the dominant one which peaked up to 100% of the total FPs in 6

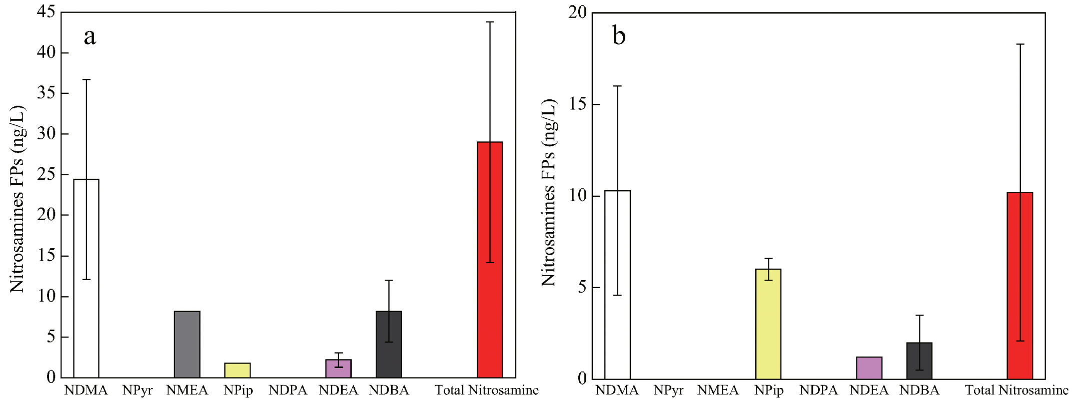

Fig. 5 – Nitrosamine formation potential of river water sample (a) and ground water sample (b).

river samples and 7 ground water samples. The concentration of NDMA after chlorination was much higher than that of the corresponding source water in 16 river water samples and 8 ground water samples, the increased concentration could be related to the formation of chloramine due to the existence of high level of ammonia in water (0.02–8.96 mg/L) (Wang et al., 2011; Van Huy et al., 2011). On the other hand, the decreased of the concentration of NDMA was observed in 7 ground water samples (G3, G6, G7, G9, G16, G17, G21), this phenomenon may attribute to the lack of nitrosamine precursor and the reaction of nitrosamines with chlorine or other compounds existed in water samples. Further studies are necessary to clarify the reduction mechanisms. Similarly with NDMA, there is no change in the same trend of the concentration of NDBA and NDEA after chlorination. NDBA-FP was found relatively higher (1.2–9.0 ng/L) than the concentrations of NDBA in the corresponding river water samples from most sample sites except for site R5, R6, R7 and R13 where NDBA were reduced by 4.4, 32.0, 0.8 and 2.2 ng/L, respectively.

Since the NDMA-FP was the most frequently detected nitrosamines, the linear correlations between measured basic water quality parameters (e.g., DOC, UV_{254}, TDN, NH_4-N) and NDMA-FP were examined to see if there is any parameter which may be used to predict NDMA precursor levels. As

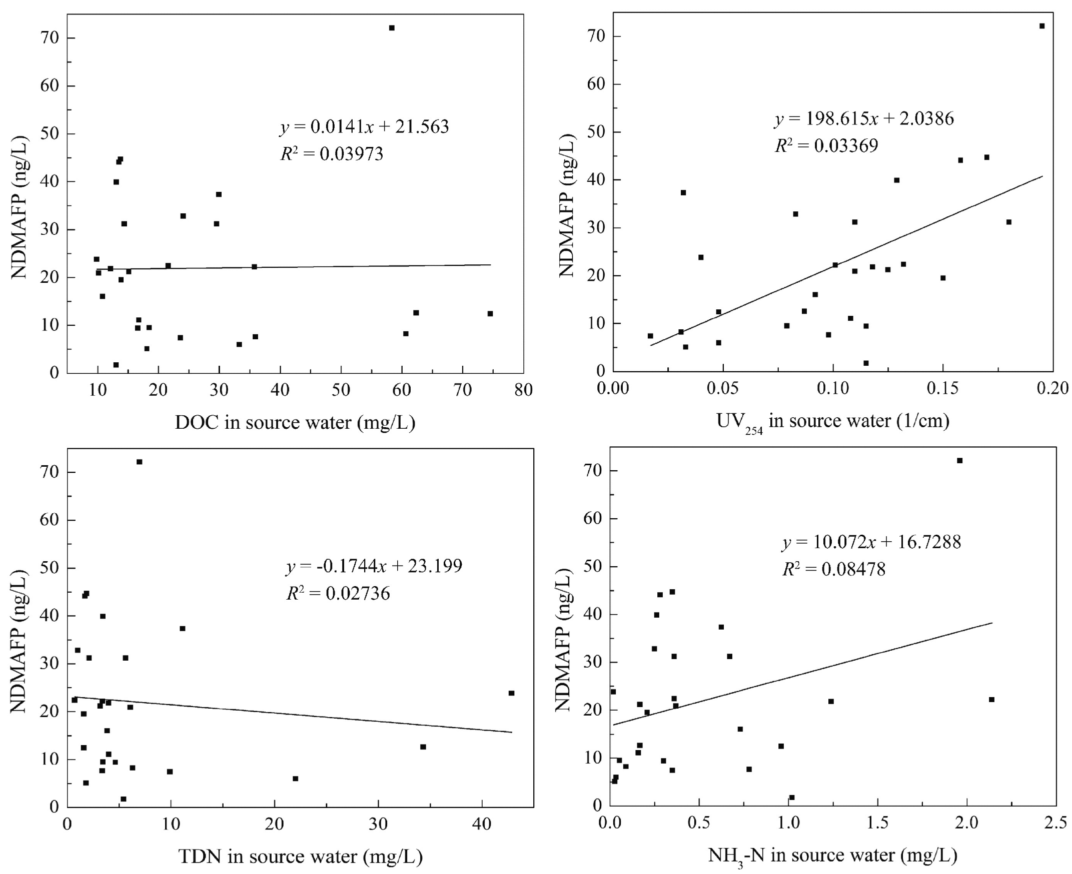

Fig. 6 – Linear relationship analysis of nitrosamine precursors with basic water quality parameters.

shown in Fig. 6, poor correlation ($R^2 < 0.1$) was observed between the NDMA-FP and NH3-N, DOC, and TDN. However, UV_{254} showed better relationship with NDMA-FP ($R^2 = 0.3369$) which indicated that UV_{254} may correlate with NDMA-FP. This correlation was in accordance with the previous study by Krasner et al. (2013), but was inconsistent with the previous studies (Asami et al., 2009; Wang et al., 2016), which showed that the NDMA-FPs were closely linked to ammonia values in source waters but weaker correlations for UV_{254}. In general, an accurate relationship may not be observed due to the lower concentration (ng/L level) of NDMA compared with the higher concentration levels of water quality parameters (mg/L level); further, the precursors of NDMA at lower concentration may significantly influence the NDMA-FPs, and which could not be reflected by the basic water quality parameters. Further studies are necessary to clarify the relationship between NDMA-FP and the basic water quality parameters.

3. Conclusions

Nitrosamines were widely detected from both surface and ground water samples taken along the Songhua River. NDMA was obviously the most frequently detected nitrosamine and was present in the highest concentrations in both surface and ground water samples. Contributing to the biodegradation and dilution, the nitrosamines' concentration at downstream is always lower than that of midstream. The concentration of some species of nitrosamine increased while some species decreased after chlorination, and further studies are necessary to clarify the corresponding mechanism. UV_{254} showed a better relationship with NDMA-FP rather than DOC, NH4-N, and TDN.

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