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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. 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.

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; 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 (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.-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 carcinogens to

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humans (Group 2B) (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 in 2009. (Q6) 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. (Q7) HPLC 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.

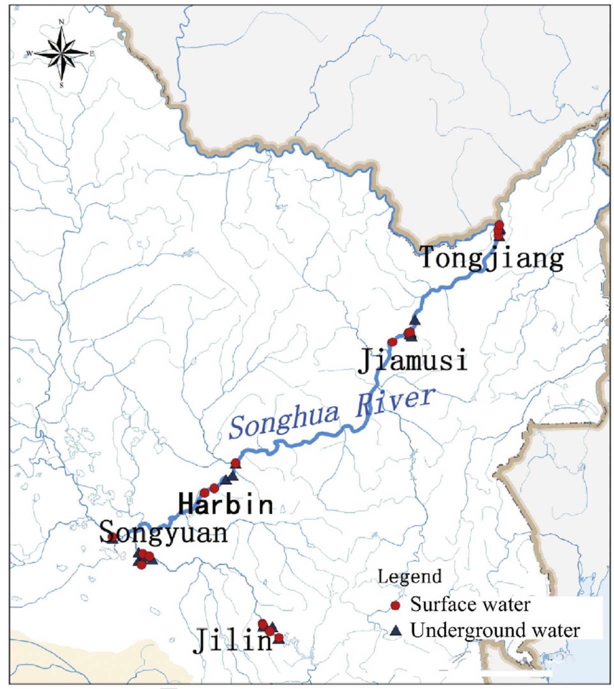

Fig. 1 – Map of sampling sites along the Songhua River.

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 (Q8) 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 nitrosamine separation. The mobile phase was composed of

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