# Occurrence and Source of Nitrosamines and Secondary Amines in Groundwater and its Adjacent Jialu River Basin, China

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S Supporting Information

ABSTRACT: The presence of mutagenic and carcinogenic nitrosamines in groundwater is of great concern. In this study, eight nitrosamines including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosomorpholine (NMOR), N-nitrosopiperidine (NPIP), N-nitrosodi-n-propylamine (NDPA), and N-nitrosodi-n-butylamine (NDBA) and corresponding secondary amines were investigated in shallow groundwater, river water, and wastewater samples collected from the Jialu River basin. The total concentrations of nitrosamines and secondary amines in groundwater were ND−101.1 ng/L and 0.36−4.38 μg/L, respectively. NDMA and its secondary amine DMA (44.7%/ 40.1%) were the predominant compounds in groundwater, followed by NDEA/DEA (21.7%/29.3%) and NDBA/DBA (26.4%/ 27.4%). Relatively high concentrations of these six compounds were also observed in river water that was influenced by the direct discharge of industrial and domestic wastewater. Using acesulfame as a quantitative population marker, the contribution of domestic sources to the concentrations of nitrosamines and secondary amines was 39−85% in downstream reaches of the Jialu River, and that of industrial sources was estimated to be 65−98% in other sites of the area. Both on-site leakage of domestic and industrial wastewater and leaching from river water would contribute to the occurrence of target pollutants in groundwater. The target pollutants posed a cancer risk of 4.12×10^{-5} to the local populations due to the direct usage of groundwater as potable water.
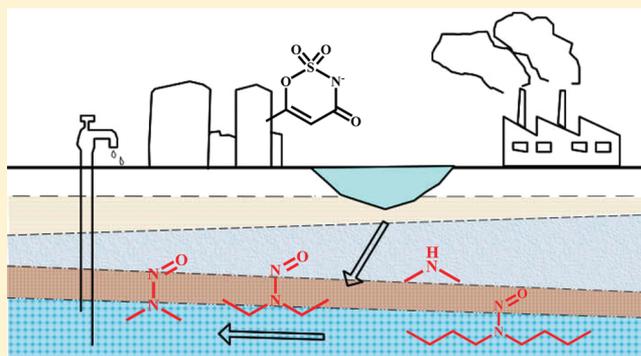
INTRODUCTION

Nitrosamines are carcinogenic to multiple organs in at least 40 animal species including higher primates,[1] and epidemiologic evidence has also correlated dietary intake of nitrosamines with the risk of stomach, esophageal, and nasopharyngeal cancers.[2] It is estimated that concentrations of N-nitrosodiethylamine (NDEA) as low as 0.2 ng/L in drinking water would be associated with a 10^{-6} lifetime cancer risk.[3] The International Agency for Research on Cancer has classified N-nitrosodimethylamine (NDMA) and NDEA as probable carcinogens to humans (Group 2A), and N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosomorpholine (NMOR), N-nitrosopiperidine (NPIP), N-nitrosodi-n-propylamine (NDPA), and N-nitrosodi-n-butylamine (NDBA) are classified as possible carcinogens to humans (Group 2B).[4]

As an emerging disinfection byproduct of chlorination, chloramination,[5−9] and ozonation[9−11] in water treatment processes, NDMA has been widely investigated in drinking water in many countries, including Canada,[12,13] the United States,[14] Japan,[15] and China.[16] In some developing countries, shallow groundwater is the main source of drinking water due to a lack of safe drinking water and water treatment systems.[17−20] In view of the high water solublility and negligible soil adsorption of nitrosamines, a high-leaching potential from

surface water to groundwater can be expected as simulated in a previous paper.[21] Therefore, the occurrence of nitrosamines in groundwater is of great concern. High concentrations of NDMA have been reported in areas near rocket engine testing facilities in California (up to 400 μg/L) due to the microbiological conversion of the unsymmetrical dimethylhydrazine (UDMH)-based rocket fuels.[14] NDMA was also present at high concentrations (up to 600 ng/L) in locations where chlorinated wastewater effluent was used for aquifer recharge.[22] A recent study has also reported concentrations of NDMA ranging from <0.5 to 5.2 ng/L in groundwater that had no specific sources of pollution.[23] Whereas NDMA was the only nitrosamine analyzed in all these investigations, there are no reports of the occurrence of other nitrosamines in groundwater despite the fact that these compounds have been widely detected in surface water and effluent of wastewater treatment plants.[16,24,25] In addition, concentrations of secondary amines in the μg/L range have been detected in surface waters.[26−28] Ingestion of secondary amines can lead to

the endogenous formation of nitrosamines due to the presence of nitrite in the human stomach.[29−31] Because secondary amines (log K_{ow} −0.86 to 2.8) exhibit polarity similar to that of nitrosamines (log K_{ow} −0.57 to 2.63),[32] the occurrence of secondary amines in groundwater should also be of concern. Therefore, it is necessary to investigate the occurrence of various nitrosamines and secondary amines in groundwater to better assess the potential health risks to humans, in particular for populations that use groundwater as their main source of drinking water.

The on-site leakage from decrepit sewer pipes and sewage recharge and infiltration by contaminated surface water are the main sources of groundwater pollution.[33,34] The occurrence of NDMA in groundwater indicates that industrial and domestic discharge of nitrosamines cannot be neglected.[14,22] Nitrosamines can be formed unintentionally from a range of industrial processes such as rubber manufacturing and processing, leather tanning, metal casting, and food processing.[35,36] Secondary amines are used in large quantities as important intermediates in the chemical and pharmaceutical industries.[28] Nitrosamines and secondary amines can also be discharged into the aquatic environment via domestic sources as previous studies have found relatively high concentrations of nitrosamines in urine samples[24,37−40] and sewer trunk lines.[41] Secondary amines can also be formed via biodegradation of proteins and nitrogen-containing compounds in domestic wastewater.[28] Therefore, source analysis of nitrosamines and secondary amines can help protect groundwater quality.

The Jialu River, which is an important tributary of the Huaihe River, is impacted by the direct discharge of industrial and domestic wastewater. In recent decades there has been an increasing incidence of digestive system cancer among local residents and it is suspected that this is related to the consumption of untreated shallow groundwater as the main source of drinking water.[42−44] As one group of the classic digestive system carcinogens, eight nitrosamines (NDMA, NMEA, NPYR, NPIP, NMOR, NDEA, NDPA, and NDBA) and their corresponding secondary amines (dimethylamine (DMA) methylethylamine (MEA), pyrrolidine (PYR), piperidine (PIP), morpholine (MOR), diethylamine (DEA), di-n-propylamine (DPA), and di-n-butylamine (DBA)) were investigated in the Jialu River basin and corresponding shallow groundwater along the river basin. Then source analysis of nitrosamines and secondary amines was carried out using acesulfame as a molecular marker. The results obtained in this study are expected to be used for causal analysis of the increasing incidence of digestive system cancer in this region.

■ MATERIALS AND METHODS

Sample Collection. The study areas and sampling sites are shown in Figure 1. The Jialu River and its tributaries cover most of the residential and industrial areas of Weishi and Fugou county, Henan Province, China. The digestive system cancer incidence (carcinoma of the esophagus, stomach, and liver) in 2004−2006 was reported to be 6.1×10^{-4}, which was 1.71-fold of that reported in 1973−1975 in this area.[45] This area is about 2500 km^2 with a total population of 1.38 million inhabitants. Many kinds of industries such as tanneries, rubber plants, perfumery plants, and chemical industries were located in this area, and domestic and industrial wastewaters were discharged without treatment due to the lack of wastewater treatment plants. In November 2010, January 2011, and March 2011, grab water samples were collected from 22 sites on the Jialu River
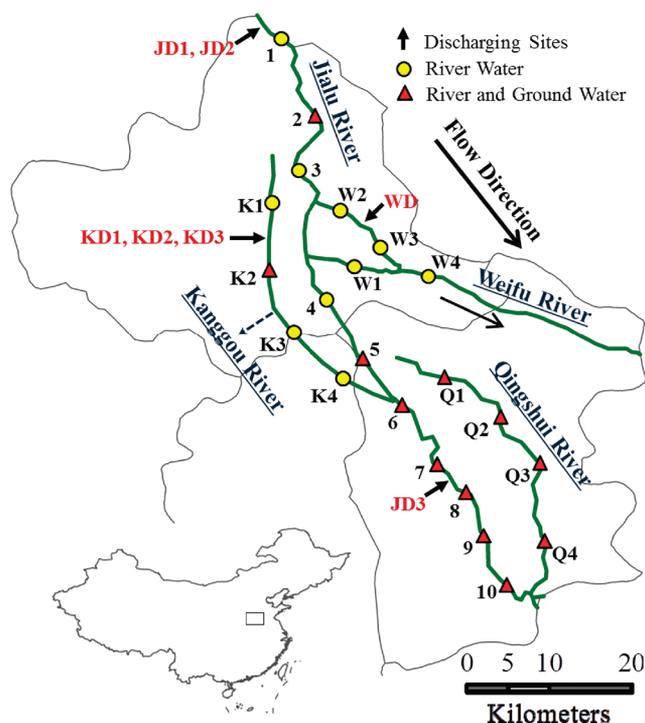

Figure 1. Map of sampling sites in the Jialu River basin.

and its tributaries, and 7 grab wastewater samples were taken from all the visible discharge sites along the rivers. The wastewaters at sites KD2 and WD were discharged only from industrial areas; wastewaters at sites KD1, KD3, JD1, JD2, and JD3 were from domestic sources. Wastewater at site JD3 was collected at the sewerage canal into the river, while other wastewaters were collected from locations near the industrial or residential areas. Most inhabitants have wells supplying drinking water at home, and groundwater is directly used as potable water. The groundwater from wells receives river water in the basin since the river water level is higher than groundwater table in this area, and the on-site leakage of wastewater is also a possible source of groundwater due to lack of wastewater treatment facilities in this area. During the three sampling periods, grab groundwater samples from wells were also collected from 12 sites that were less than 2 km away from the corresponding river water sampling sites. All the groundwater samples were collected from wells with depth less than 30 m (shallow aquifers), and the detailed information of each site is given in Table S1. There was no rainfall during the sampling periods and at least one week before the sampling date. All samples were collected in amber glass bottles and filtered with a glass microfiber filter (GF/C, 1.2 μm; Whatman, Maidstone, UK) before being extracted on the day of collection.

Sample Preparation for Analyzing Nitrosamines. After filtration, 0.5 L of water was adjusted to pH 8.0 with about 1 g of solid sodium bicarbonate and spiked with 20 ng/L internal standards (NDMA-d_6, NMEA-d_3, NPYR-d_8, NMOR-d_8, NDEA-d_{10}, NPIP-d_{10}, NDPA-d_{14}, NDBA-d_{18}). The samples were extracted using Resprep EPA 521 cartridges (6 mL, 2 g, activated charcoal packing for NDMA, Restek, Bellefonte, PA, USA) which had been preconditioned with 10 mL of hexane, 20 mL of dichloromethane, 20 mL of methanol, and 20 mL of water at a flow rate of 3−5 mL/min. Next, the cartridges were dried under a flow of nitrogen gas. After 15 mL of dichloromethane was used to elute each cartridge, 400 μL of
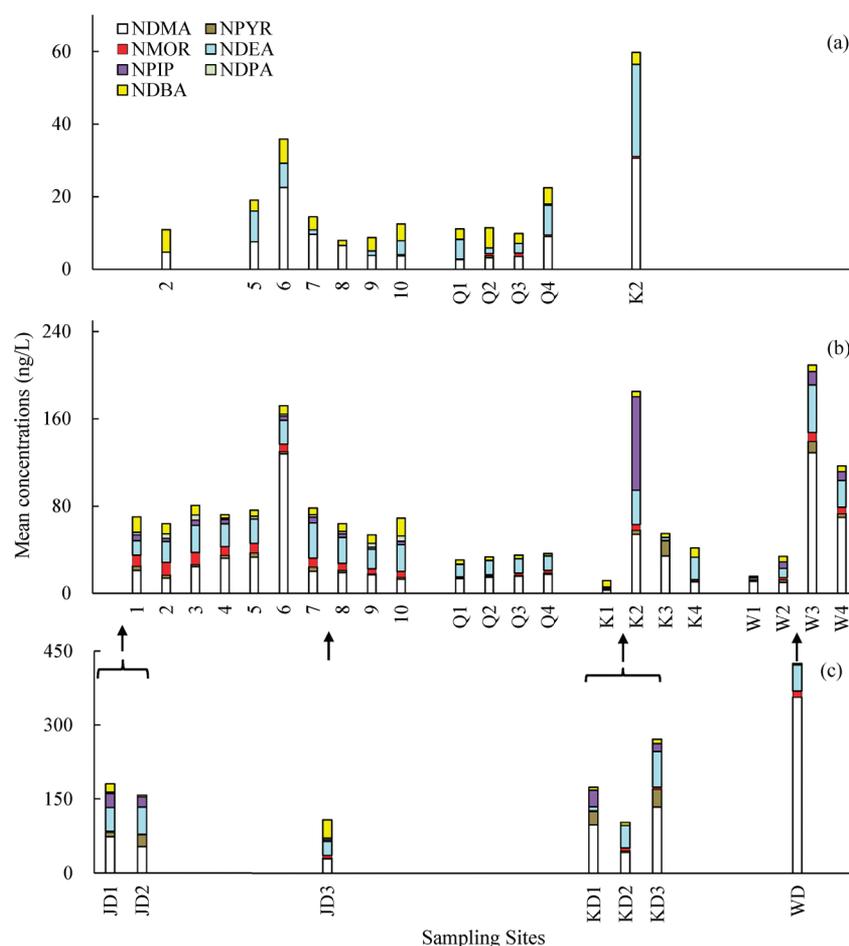
Figure 2. Concentrations of nitrosamines (ng/L) in groundwater (a), river water (b), and wastewater (c) samples collected in the Jialu River basin. The mean nitrosamines concentrations of three sampling periods were plotted.

a water/methanol solution (95:5, V/V) was added to the elutions, and the dichloromethane was completely removed using a rotary evaporator (Heidolph, Germany). Then 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 Acrodisc13 mm, 0.2 μm, PALL) prior to injection to the UPLC-MS/MS system.

UPLC-ESI-MS/MS Analysis for Nitrosamines. Nitrosamine analysis followed the method of Wang et al.[16] Briefly, the LC apparatus was an Acquity Ultra performance LC (Waters, USA). All analytes were separated using a Waters Acquity UPLC BEH C18 column (150 mm × 2.1 mm, 1.7 μm particle size; Waters, USA). Methanol (A) and ultrapure water containing 10 mmol/L ammonium bicarbonate (B) were used as mobile phases. Mass spectrometry was performed using a Premier XE tandem quadrupole mass spectrometer (Waters) equipped with a Z-Spray ionization (ESI) source. ESI-MS/MS detections were performed in the positive ion mode, and quantitative analysis was performed in the multiple reaction monitoring (MRM) mode.

Analysis of the Secondary Amines and Acesulfame in Water Samples. The eight secondary amines were analyzed using GC/MS after derivation with benzenesulfonyl chloride (BSC) according to the method reported by Sacher et al.[28] The acesulfame was analyzed using LC-MS/MS. Details are given in the Supporting Information.

Quality Assurance and Quality Control. Concentrations and recoveries are represented as "arithmetic mean ± standard deviation". Concentrations of nitrosamines and secondary amines were quantified by the internal standard isotope-dilution method using the mean relative response factors determined from standard calibration runs. The absolute recoveries of deuterated nitrosamines and DMA-d_6 were 52 ± 6 to 97 ± 11% and 85 ± 6%, respectively (Table S2). Nitrosamines were quantified relative to their corresponding deuterated nitrosamines, and secondary amines were quantified relative to DMA-d_6. The relative recoveries for all target analytes (corrected for internal standards) were 87 ± 13 to 111 ± 9% (Table S3). All equipment was rinsed with methanol to avoid contamination, and dichloromethane was distilled at 47 °C before use to remove any residual nitrosamines in the solvent. A laboratory blank was incorporated into the analytical procedures for every batch of 10 samples. Nitrosamines and secondary amines were not detected in blanks, and the method detection limits (MDL) were set to the instrumental minimum detectable amounts. The MDLs of nitrosamines were from 0.2 (NDBA) to 0.8 ng/L (NDMA), and the MDLs of secondary amines were from 0.04 (PYR) to 0.1 μg/L (DMA) in water samples. For those results less than the MDL, half of the MDL was assigned to avoid missing values in statistical analyses.
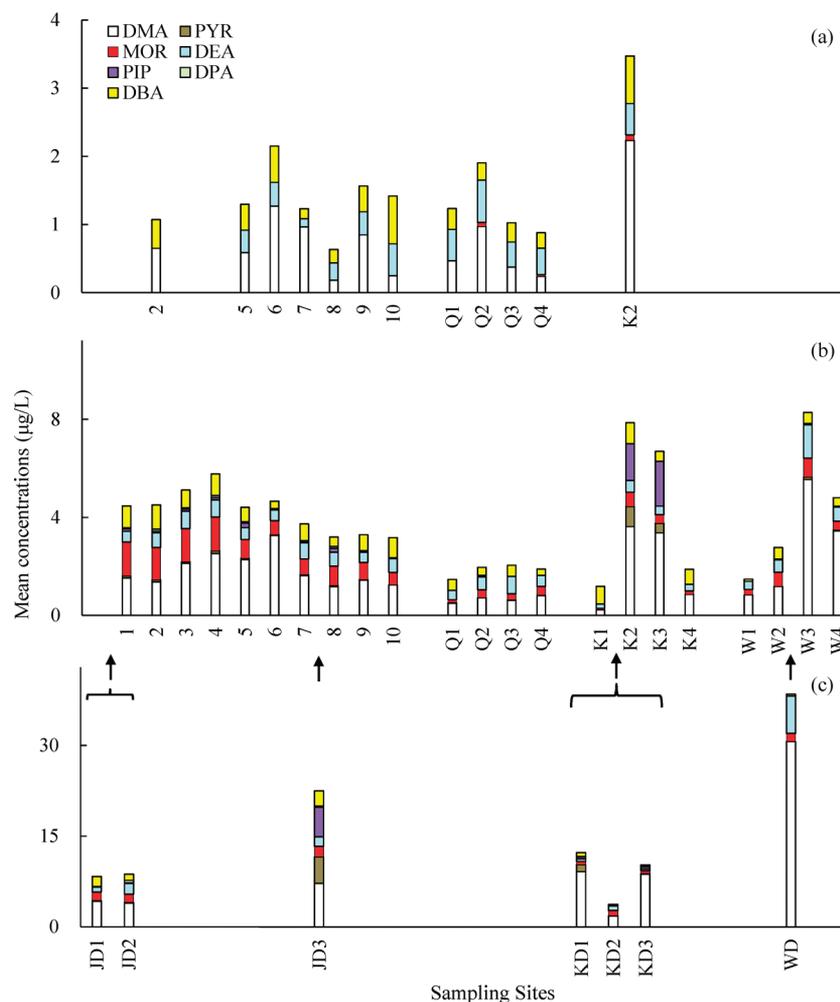
Figure 3. Concentrations of the secondary amines (μg/L) in groundwater (a), river water (b), and wastewater (c) samples collected in the Jialu River basin. The mean secondary amines concentrations of three sampling periods were plotted.

RESULTS AND DISCUSSION

Occurrence of Nitrosamines and Secondary Amines. *Shallow Groundwater.* Six nitrosamines including NDMA, NDEA, NMOR, NDBA, NDPA, and NPYR were detected in groundwater samples collected from twelve sites as shown in Figure 2a. NDMA was detected in 77% of the groundwater samples with an average concentration of 9.8 ± 12.7 ng/L, accounting for 44.7 ± 25.6% of the total nitrosamines. NDMA was the only compound investigated in groundwater samples in previous studies,[14,22,23] and the concentrations of NDMA in the current study were higher than those in groundwater collected in Tokyo, Japan (<0.5−5.2 ng/L)[23] but lower than those in groundwater affected by water reclamation plants (WRPs) in the U.S. (up to 600 ng/L).[22] The detection frequencies of other nitrosamines including NDEA, NMOR, NDBA, NDPA, and NPYR were 67%, 23%, 93%, 10%, and 13%, respectively, and the mean concentrations were 6.4 ± 13.0, 0.3 ± 0.5, 4.0 ± 3.2, 0.1 ± 0.1, and 0.3 ± 0.2 ng/L, respectively. To our knowledge, this is the first report concerning the occurrences of nitrosamines other than NDMA in groundwater. Relatively high contributions of NDEA (21.7 ± 18.9%) and NDBA (26.4 ± 22.8%) to the total nitrosamines were observed. The maximum concentration of NDEA (68.4 ng/L) in groundwater was even higher than those in the source water of drinking water treatment plants in

China (1.9−16.3 ng/L)[16] and in influents and effluents from 20 sewage treatment plants (STPs) in Switzerland (up to 25 ng/L),[24] and this compound has a greater carcinogenic potential (10⁻⁶ lifetime cancer risk level: 0.2 ng/L) than NDMA (0.7 ng/L) in the quantitative estimate of carcinogenic risk from drinking water.[3] The concentrations of NDBA (up to 15.8 ng/L) were comparable with those in the source water of drinking water treatment plants in China (1.9−16.3 ng/L)[16] and wastewaters in Switzerland (median value: 6 ng/L),[24] suggesting that these pollutants should not be neglected in future investigations.

Four secondary amines including DMA (0.79 ± 0.88 μg/L), MOR (0.04 ± 0.03 μg/L), DEA (0.38 ± 0.24 μg/L), and DBA (0.38 ± 0.28 μg/L) were detected in groundwater with detection frequencies of 90%, 17%, 97%, and 100%, respectively (Figure 3a). Consistent with the nitrosamines, the corresponding secondary amines DMA (40.1 ± 23.2%), DEA (29.3 ± 15.5%), and DBA (27.4 ± 13.8%) accounted for relatively high contributions to the total secondary amines. The levels of these secondary amines in groundwater were comparable with those in drinking water and river water reported in previous papers.[16,26−28]

River Water. Of the eight nitrosamines investigated, NDMA (31.7 ± 49.5 ng/L), NDEA (19.5 ± 16.8 ng/L), NMOR (5.5 ± 6.0 ng/L), NDBA (6.2 ± 4.6 ng/L), NPYR (2.8 ± 2.7 ng/L),

NPIP (7.3 ± 34.1 ng/L), and NDPA (1.7 ± 2.4 ng/L) were detected in river samples with a detection frequency of 98%, 97%, 95%, 100%, 95%, 23%, and 61%, respectively (Figure 2b). NDMA and NDEA were also the most abundant compounds detected in river samples, accounting for 40.5 ± 18.4% and 28.0 ± 13.0% of the total concentrations of nitrosamines, respectively. In previous investigations, NDMA was the major nitrosamine quantified in surface water.[16,22,23,25] Except for the surface water (about 50−600 ng/L) affected by WRPs in Los Angeles County, California,[22] the concentrations of NDMA in river samples in the current study (up to 334.9 ng/L) were much higher than those in surface water in China (6.4−13.9 ng/L),[16] five rivers in Tokyo (<0.5−3.4 ng/L),[23] and the Quinnipiac River in the U.S. (4−32 ng/L).[25] This indicates relatively high pollution of nitrosamines in river water from the Jialu River basin.

With the exception of MEA, each of the secondary amines corresponding to the nitrosamines investigated was detected in river water samples (Figure 3b). Concentrations of DMA, DEA, MOR, DBA, PYR, PIP, and DPA were 1.78 ± 1.51, 0.54 ± 0.29, 0.66 ± 0.55, 0.57 ± 0.48, 0.09 ± 0.28, 0.17 ± 0.53, and 0.05 ± 0.04 μg/L, respectively. DMA (43.3 ± 15.0%) and DEA (16.6 ± 8.5%) were the greatest contributors to the total concentration of secondary amines. Consistent with the concentration of NDMA, the maximum concentration of DMA (7.21 μg/L) in the current study was much higher than those in the river Elbe (<3 μg/L), Germany[28] and similar to those in effluents of seven STPs in California (<10 μg/L).[41] Furthermore, significant positive relationships were obtained between the concentrations of NDMA, NDEA, NMOR, NDBA, NPYR, NDPA, and the corresponding secondary amines (p <0.001) (Figure S1), suggesting that these compounds were likely to originate from common sources.

Wastewater. In addition to the river water samples, 7 wastewater samples collected from discharging sites in the Jialu River basin were analyzed for concentrations of nitrosamines and their corresponding secondary amines (Figure 1). Concentrations of nitrosamines (82.0−607.9 ng/L) and secondary amines (2.20−53.19 μg/L) at the 7 discharging sites were higher than those in river water samples. There was an abrupt increase in the concentrations of target pollutants at sampling sites K2 and W3 downstream of the discharging sites (KD1, KD2, KD3, and WD), while the concentrations did not increase at sampling site 8, which was possibly due to the low wastewater flow at site JD3. The profiles of nitrosamines and secondary amines in the discharging wastewaters were also similar to those in the river water samples collected downstream from the discharging sites. These results indicate the influence of wastewater on the load of nitrosamines and secondary amines in this area. To clarify the types of wastewater samples, the artificial sweetener, acesulfame, was quantified as a molecular marker of domestic wastewater input. Acesulfame is consumed in considerable quantities and excreted via urine and feces from humans, and it has been proved to be an ideal molecular marker of domestic wastewater input since the compound solely comes from domestic sources and is conserved in the environment.[46] As illustrated in Figure 4, concentrations of acesulfame in wastewater from sites KD2 and WD (0.25−1.24 μg/L) were much lower than those in wastewater samples (8.1−50.0 μg/L) collected from sites KD1, KD3, JD1, JD2, and JD3, which is consistent with the wastewaters at sites KD2 and WD being discharged from

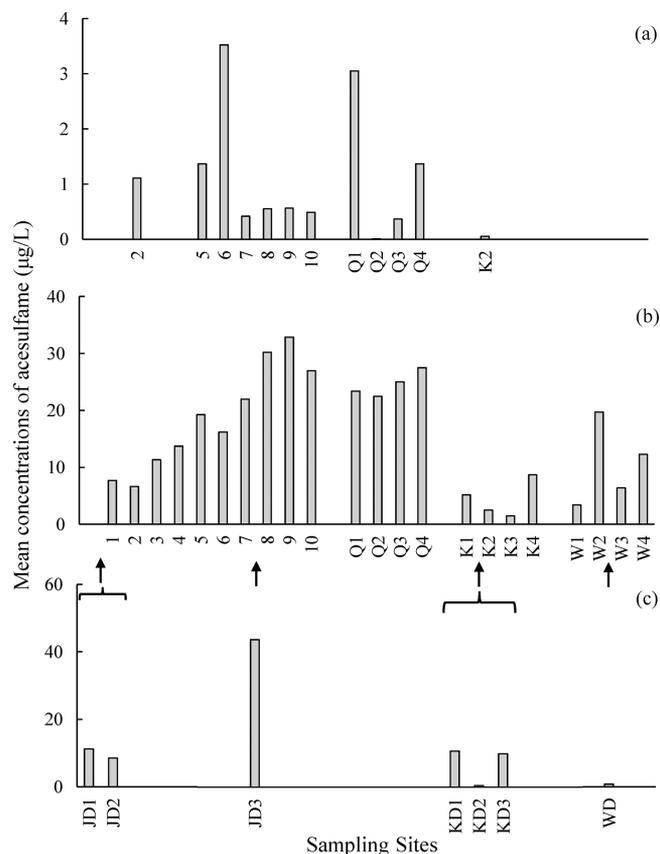**Figure 4.** Concentrations of acesulfame (μg/L) in groundwater (a), river water (b), and wastewater (c) samples collected in the Jialu River basin. The mean acesulfame concentrations of three sampling periods were plotted.

industrial areas, whereas the wastewaters at sites KD1, KD3, JD1, JD2, and JD3 were influenced by domestic sources.

Source Analysis. *River Water.* Because acesulfame is a quantitative marker of domestic wastewater, an attempt was made to estimate the source contribution to the occurrence of nitrosamines and secondary amines in river water samples based on concentrations of acesulfame. Previous studies have found a good linear correlation between concentrations of acesulfame and the population (P) in the catchment area per throughflow of water (Q, m^3/s) (P/Q, person/m^3/s).[46] Therefore, it is possible to utilize acesulfame as a population marker of the discharged domestic waste in order to estimate the levels of nitrosamines and secondary amines in river water that originated from domestic sources. Theoretically, the ratios of concentrations of nitrosamines/secondary amines and acesulfame should be constant in areas only affected by domestic wastewater (control area). Thus, in areas affected by both domestic and industrial sources, the load (D) of the pollutants contributed by domestic sources can be calculated using the ratios between concentrations of nitrosamines/secondary amines and acesulfame in the control area using eq 1:

$$D(\%) = \left(C_{AR} \times \frac{C_P}{C_A} \right) / C_{PR} \tag{1}$$

The contribution from industrial sources (I) is calculated by eq 2:

$$I(\%) = 1 - D \qquad (2)$$

where C_A and C_P are the concentrations of acesulfame and pollutants, respectively, in surface water that originated solely from domestic sources, and C_{AR} and C_{PR} are the concentrations of acesulfame and pollutants, respectively, in surface water affected by domestic and industrial sources.

Considering the biodegradation and/or photolysis of nitrosamines/secondary amines in surface water,[47,48] concentration ratios between the pollutants and acesulfame in domestic wastewaters would be inappropriate to be used as reference values. The Qingshui River flows through a residential area, and the river water was only affected by the local domestic sewage since no industrial activities were observed along the river. As shown in Figure 4, the concentrations of acesulfame (20.97–30.12 μg/L) were relatively high and constant at sites Q1–Q4 along the Qingshui River, and the ratios between pollutants and acesulfame were also constant (1.31–1.48 ng/μg for nitrosamines and 0.063–0.087 μg/μg for secondary amines). Thus, using eqs 1 and 2, the contributions of nitrosamines and secondary amines from domestic and industrial sources to the river water collected from the Jialu, Kanggou, and Weifu Rivers were calculated, although such estimation may be slightly underestimated or overestimated considering the possible site-specific variations of biodegradation and photolysis rates in surface water.[47,48] As shown in Figure S2, the contribution of industrial sources to nitrosamines and secondary amines increased to 94–98% after the discharge of wastewater into the Kanggou and Weifu Rivers (at sites K2 and W3). In the upstream reaches of the Jialu River (sites 1–6), nitrosamines and secondary amines were mainly from the industrial discharges with contributions ranging from 65 to 89%, while domestic sources became more important at the downstream reaches of the Jialu River (sites 7–10) with contributions of 39–85%.

Shallow Groundwater. Previous studies have demonstrated that nitrosamines and secondary amines have a high-leaching potential in subsurface systems and biodegradation was the major attenuation mechanism of nitrosamines in groundwater-recharge systems.[21,22] Considering the different biodegradation rates of nitrosamines and secondary amines,[21,49,50] the concentration ratios between the total concentrations of pollutants and acesulfame as used in river water would be inappropriate for estimating the source contributions in groundwater. It was noted that NDMA and acesulfame have similar biodegradation rates in soils (half-lives: 4–39 days for NDMA[51,52] and 3–49 days for acesulfame[53]). And sorption of acesulfame to soils or sediments was negligible due to its higher solubility (log K_{OW} −1.33) compared with NDMA (log K_{OW} −0.57, log K_{OC} 1.07).[32] Therefore, the concentration ratios of NDMA to acesulfame were calculated to explore the potential sources of target pollutants in groundwater. It was found that the concentration ratios of NDMA to acesulfame in groundwater were much higher than those in river water except for sites 2, 6, and Q1, but similar to those in domestic or industrial wastewater (Figure 5). The relatively low concentration ratios in surface water and wastewater at site JD3 (sewerage canal) were possibly due to the photolysis of NDMA in surface water (photolysis half-lives ranged from hours to a few days).[47] The concentration ratios in groundwater from sites 2, 6, and Q1 were similar to those of surface water, suggesting that the
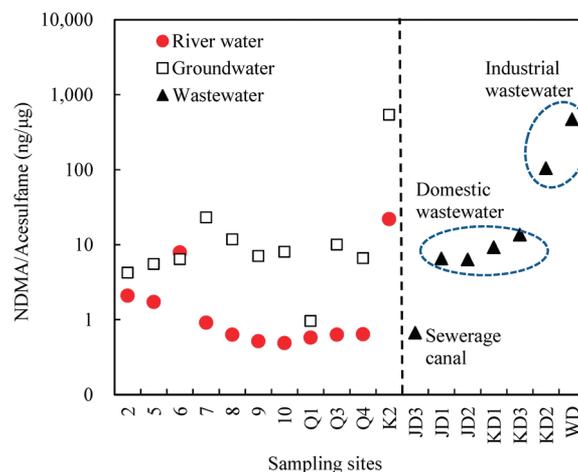

Figure 5. Concentration ratios of NDMA to acesulfame in river water, groundwater, and wastewater.

pollutants in groundwater from these sites would be leached from the corresponding river water. The concentration ratios in groundwater from sites Q3, Q4, and 8–10 were similar to those of domestic wastewater (JD1, JD2, KD1, and KD3), and that from site K2 was similar to those of industrial wastewater (KD2 and WD), suggesting that on-site leakage from domestic and industrial wastewater would contribute to the pollution in groundwater at these sites.

Risks. Nitrosamines and secondary amines, especially NDMA, NDEA, NDBA, and their corresponding secondary amines (DMA, DEA, DBA), were often detected in groundwater, which would pose a cancer risk to populations using groundwater as drinking water source in this area. Because the cancer potencies of nitrosamines are available, we made an attempt to estimate the cancer risk (R_i) due to the ingestion of groundwater containing NDMA, NDEA, and NDBA as quantified using eq 3

$$R_i = 1/10000 \times \sum_{j=1}^{j=10000} C_{ij} \times Baseline_i \qquad (3)$$

where the subscript i represents the kind of chemical (NDMA, NDEA, and NDBA), C_{*j} is the average concentration of NDMA, NDEA, and NDBA in groundwater that was estimated by the bootstrap method (Matlab 2008b), j is the sampling time in the bootstrap method, and *Baseline* is the drinking water unit risk of NDMA, NDEA, or NDBA. Different unit risks have been reported by WHO[54] and U.S. EPA, and the unit risks of U.S. EPA were used in this study: 1.4×10^{-3} per (μg/L) for NDMA, 4.3×10^{-3} per (μg/L) for NDEA, and 1.6×10^{-4} per (μg/L) for NDBA.[3] The estimated cancer risks for NDMA, NDEA, and NDBA were 1.36×10^{-5}, 2.70×10^{-5}, and 0.06×10^{-5}, respectively. Considering the similar mechanism of carcinogenesis of these chemicals, the sum of the cancer risk from each nitrosamine was considered as the total cancer risk, which was determined to be 4.12×10^{-5} (95% CI: 2.44×10^{-5} to 6.48×10^{-5}). This risk is higher than a cancer risk of 10^{-5} which is the default acceptable level.[55]

Overall, the discharge of both industrial and domestic wastewater contributed to the load of the target pollutants in the environment. The pollution of groundwater in the Jialu River basin by nitrosamines may pose a risk of developing cancer of 4.12×10^{-5} to local populations using groundwater as

drinking water. These results provide important information that demonstrates the need for effective control of these pollutants in areas with a high incidence of digestive system cancer.

ASSOCIATED CONTENT

ⓢ Supporting Information

Text, figures, and tables addressing (1) reagents, instrument analysis for secondary amines and acesulfame; (2) correlation between nitrosamines and corresponding secondary amines in surface water of Jialu River basin; (3) calculated contributions of domestic and industrial sources to the nitrosamines and secondary amines load in river samples; (4) characteristics of groundwater; (5) absolute recoveries of deuterated nitrosamines and secondary amines in various types of aqueous matrices; (6) relative recoveries of eight secondary amines in various types of aqueous matrices; (7) concentrations of nitrosamines, secondary amines, and acesulfame in groundwater, river water, and discharging site samples in Jialu River Basin. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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