Concentration level and geographical distribution of nitrobenzene in Chinese surface waters

GAO Jijun[1,2], LIU Linghua[2], LIU Xiaoru[2], ZHOU Huaidong[2],
WANG Zijian[1,*], HUANG Shengbiao[1]

1. State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: gaojj@iwhr.com
2. Department of Water Environment, The Institute of Water Resource and Hydropower Research, Beijing 100038, China

Abstract

Nitrobenzene was reported to occur at relatively high concentrations in some Chinese surface water and to cause an environmental pollution event in 2005. To map the distribution of nitrobenzene in the Chinese surface water throughout China, surface water samples were collected from over 600 sites in the 7 major watersheds and three drainage areas. The samples were analyzed for concentration of nitrobenzene. Overall, nitrobenzene was more frequently detected at higher concentrations in the rivers of North China, including Songhua River, Liaohe River, Haihe River, Yellow River, Huaihe River, and Northwest drainage area rivers, compared with those in the rivers of South China, including Yangtze River, Pearl River, Southeast drainage area rivers and Southwest drainage rivers. The detection rate of nitrobenzene was 83.2% for all the samples, with a mean value of 18.1 ng/L and a range of < 0.3–8,450.0 ng/L. The highest mean concentration of nitrobenzene was observed in the Yellow River, followed by Huaihe River. The results of this investigation indicated that nitrobenzene should be of particular concern in China and its ecological and health risk should be assessed.

Key words: nitrobenzene; watershed; surface water

Introduction

Nitrobenzene is an oily yellow liquid with an almond-like odor, which is used to produce aniline, lubricating oils, dyes, drugs, pesticides, and synthetic rubber (ATSDR, 1999). It dissolves only slightly in water and will evaporate to air. Now, nitrobenzene has become a kind of important pollutant and many researchers had reported the toxicity of nitrobenzene (Cronin *et al.*, 1998; Jing and Xu, 2004; Lu, 2004; Xu and Jing, 2002; Xu and Yang, 2005). In the earlier 1980s, researchers from Japan and North America had reported the detections of nitrobenzene in the surface water (Yamagishi and Miyazaki, 1981; Yurawecz and Purna, 1983). In China, the previous work showed that nitrobenzene pollution prevailed in the surface water (Kang *et al.*, 2001; Li and He, 2006; Tian and Shu, 2003; Wang *et al.*, 2002; Wang *et al.*, 2003). However, there were only limited field investigations for nitrobenzene concentration for Chinese surface water and there is no data on spatial distribution at the national scale. For this reason, we carried out the study aiming at map the distribution of nitrobenzene in Chinese surface water.

1 Materials and methods

1.1 Sampling

Samples were taken from the seven major watersheds, including the Yangtze River, Yellow River, Pearl River, Songhua River, Liaohe River, Haihe River, and Huaihe River. Samples were also taken from the rivers in Southeast, Northwest, and Southwest drainage areas. The total number of sampling sites chosen was 623, including 217 reservoirs, and 406 rivers and lakes. The global positioning system (GPS) was used to locate the sampling positions.

1.2 Sample preparing

Samples were taken using pre-cleaned glass bottles, refrigerated and shipped to the laboratory. Aliquots of the sample (5.0 L) were filtered through a 0.45-μm glass fiber membrane under vacuum after returning to the laboratory and surrogate (1-chloro-3-nitrobenzene) was added. Nitrobenzene was extracted by solid phase extraction (SPE) following the published procedures (Zhou *et al.*, 2002; Zhang G *et al.*, 2002; Zhang Z L *et al.*, 2002). Briefly, the SPE cartridges were first conditioned with 10 ml of methanol followed by 2 × 5 ml of deionized water. Water samples were passed through the cartridges at a flow rate of

* Corresponding author. E-mail: wangzj@rcees.ac.cn.

6 ml/min under vacuum and nitrobenzene was eluted with 6 ml of ethyl acetate, followed by 5 ml ethyl acetate rinse of the surfaces. Residual water was removed by anhydrous Na_2SO_4 and the volume reduced by evaporation under nitrogen gas to 0.5 ml.

1.3 Chemical analysis

An Agilent 6890 GC (Agilent, USA) with a mass detector (5973N, Agilent, USA) was used for analyzing the nitrobenzene, using selected ion mode (SIM) for water samples analysis. The capillary column was HP-5MS (Agilent, USA) (30 m × 0.25 mm i.d. × 0.25 μm film thickness) with helium carrier gas. The temperature program was set at 60°C for 1 min, rising to 150°C at 6°C/min, then to 250°C at 15°C/min , holding for 5 min. The injector and mass spectrometer were held at 200°C and 280°C, respectively. The electronic impact energy was set at 70 eV for mass detector.

1.4 QA/QC procedures

All data were subject to strict quality control procedures. The acenaphthene-D10 was used as internal standard, and the 1-chloro-3-nitrobenzene was used as surrogate. Before sample analysis, standards were analyzed to check column performance, peak height, resolution, and method detection limit (MDL). With each set of samples to be analyzed, a solvent blank, a standard and a procedure blank were run in sequence to check for background contamination, peak identification and quantification. Nitrobenzene was identified mainly by comparing the retention time with that of the standard, and comparing the mass spectrum with the standard reference spectrum. The recovery, MDL, and relative standard deviation (RSD%) for nitrobenzene were as follows: MDL was 0.3 ng/L, the mean spike recovery was 101.6%, and RSD% ranged from 1.8% to 10.6%. The surrogate was used to compensate for losses involved in the sample extraction and work-up. In addition, the errors involved in sampling were assessed by carrying out triplicate water samples at the same site. The results showed that RSD% ranged from 3.5% to 15.6%, lower than 20%. These parameters confirmed the suitability of the analytical protocols.

1.5 Statistical analysis

The values for nitrobenzene concentration lower than the method detection limits (< MDL) were substituted with zero prior to statistical analysis. To detect the difference of nitrobenzene concentrations between the North and South China, the student *t*-test was employed in this study. Software from Excel Statistics was used in this study.

2 Results and discussion

2.1 Nitrobenzene concentration

The statistical results of nitrobenzene concentrations in the Chinese surface water are summarized in Table 1. The nitrobenzene detection rate for all the samples was 83.2%, indicating nitrobenzene pollution prevailed in Chinese surface water. The concentration of nitrobenzene ranged from < 0.3 to 8,450.0 ng/L, with a mean value of 18.1 ng/L (Table 1) and the 90% percentile value of 50.0 ng/L. For the seven major watersheds and three drainage regions, the detection rates of nitrobenzene were from 0 (Southwest drainage area) to 100% (Huaihe River). For all the rivers sampled, the mean concentration of nitrobenzene in the Pearl River was the lowest (mean value is 6.5 ng/L) and the mean value in Yellow River was the highest (mean value is 218.2 ng/L). The highest nitrobenzene concentration was detected in a sample from Yellow River (8,450.0 ng/L), followed by the sample from Yangtze river (3,616.0 ng/L). The higher concentrations sites were observed mostly in North China. According to Water Quality Standard for the Surface Water (GB 3838-2002), the concentration of nitrobenzene should be lower than 17,000 ng/L. The presented data showed that there was no violation of this water quality standard. However, it showed that concentrations of nitrobenzene for some samples were close to the standard.

The available information on the nitrobenzene concentration of Chinese surface water was very limit, mainly for some sections of Huaihe River and Yellow River. Li and He (2006) reported that nitrobenzene concentration ranged from 127.5 to 26.8 ng/L at Xiaolangdi and Gaocun sampling stations in the Yellow River, compared with

Table 1 Statistical results of nitrobenzene concentrations in Chinese surface water

Watersheds	Sample number	Detection percentage (%)	Mean value (ng/L)	Min. value (ng/L)	90% (ng/L)	Max. value (ng/L)
Songhua River	40	12.5	–	< 0.3	21.0	210.0
Liaohe River	58	34.5	–	< 0.3	50.0	110.0
Haihe River	39	87.2	27.9	< 0.3	42.0	110.0
Yellow River	50	80.0	218.2	< 0.3	90.0	8,450.0
Yangtse River	150	93.3	55.2	< 0.3	34.6	3,616.0
Huaihe River	39	100	25.4	2.0	65.2	80.0
Pearl River	150	92.0	6.5	< 0.3	16.0	76.0
Southeast drainage area rivers	74	95.9	17.4	< 0.3	44.5	172.0
Northwest drainage area rivers	18	77.8	33.1	< 0.3	66.0	100.0
Southwest drainage area rivers	5	0	–	< 0.3	< 0.3	< 0.3
North China	244	69.7	63.4	< 0.3	60.0	8,450.0
South China	379	91.8	27.8	< 0.3	28.0	3,616.0
Total number of samples	623	83.2	18.1	< 0.3	50.0	8,450.0
"*t*-Test" of difference between North China and South China		$t = 1.97$	$p = 3.1 \times 10^{-6} < 0.001$			

the present work, the concentrations ranging from 0.3 to 8,450.0 ng/L in Yellow River, the both concentrations are in the same level. In the Huaihe River, the reported mean value of nitrobenzene was 2,200 ng/L (Wang *et al.*, 2002), which was obviously much higher than that observed in present study (mean value is 25.4 ng/L), which may be due to the different sampling time and sites.

2.2 Spatial distribution of nitrobenzene in Chinese surface water

The geographic nitrobenzene distribution (Fig.1) showed that the higher concentrations sites mainly occurred in the north China, including the Yellow River, Liaohe River, Huaihe River, Songhua River, and Haihe Rivers. While in the South China, the higher nitrobenzene concentrations sites were mainly found in the estuaries of the Yangtze River, Minjiang River, Jiulongjiang River, and Pear River. The distribution of chemical industries along these rivers and estuaries may explain the higher nitrobenzene concentrations. Nitrobenzene concentrations in surface water of South China were much lower than those of North China. The statistical analysis showed a significant difference between North China and South China ($t = 1.65$, $p < 0.001$), the nitrobenzene pollution in North China surface water was more serious than that in South China surface water.
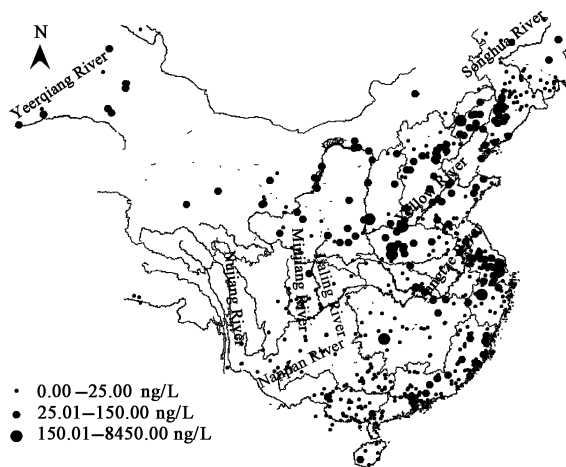

Fig. 1 Spatial distribution of nitrobenzene in the Chinese surface water.

3 Conclusions

At the national scale, the nitrobenzene mean concentration was 18.1 ng/L, with a range from < 0.3 ng/L to 8,450.0 g/L, and all the nitrobenzene concentrations were below the Surface Water Quality Standard of China. The nitrobenzene pollution in the surface water of North China was more serious than that in the surface water of South China. The higher nitrobenzene concentrations sites mainly occurred in the Yellow River, Huaihe River and several estuaries of South China, so these watersheds and regions were of particular concern and should be given priority for pollution prevention and treatment.

References

ATSDR (Agency for Toxic Substances and Disease Registry), 1999, ToxFAQs™ for Nitrobenzene.

Cronin M T D, Gregory B W, Schultz T W, 1998. Quantitative structure-activity analysis of nitrobenzene toxicity to tetrahymena thermophila. *Chemical Research in Toxicity*, 11: 902–908.

GB 3838-2002, 2002. Environmental Quality for Surface Water. Environmental Protection Agency, China.

Jing T S, Xu J, 2004. Quantitative structure-activity relationships for toxicity of nitrobenzenes to *Escherichia coli* and *Bacillus subtilis*. *Journal of Jilin University* (Science Edition), 42: 130–134.

Kang Y H, Gong Z Y, Wang Z J, Li G G, 2001. The study of VOCs in Guanting Reservoir and Yongdinghe River. *Acta Scientiae Circumstantiae*, 21(4): 338–343.

Li X R, He M C, Sun Y, Xia X H, Yan Y, 2006. Distribution of nitrobenzenes in the Yellow River from Xiaolangdi to Gaocun Research. *Environmental Science*, 27: 513–518.

Lu G H, 2004. Quantitative structure-toxicity relationship for acute toxicity of nitrobenzenes to Daphnia carinata. *Journal of Hehai University*, 32: 372–375.

Tian H J, Shu W Q, 2003. Organic pollutants in source water in Jialing River and Yangze River (Chongqing Section). *Resources and Environmental in the Yangtze Basin*, 12: 118–123.

Wang Z J, Lu Y B, Wang Y, 2002. Assessing the ecological risk of substituted benzenes in Huaihe River, China. *Acta Scientiae Circumstantiae*, 22: 300–304.

Wang H, Yang N Y, Shen Y W, 2003. Safety assessment on several organic pollutants of the Haihe River watershed. *Research of Environment Sciences*, 16: 35–36.

Xu J B, Jing T S, 2002. QSAR studies on the toxicity of nitrobenzenes to population growth of *Tereahymena pyriformis*. *Chemical Research*, 18: 258–261.

Xu J B, Yang L, 2005. SCGE stuty on DNA damage of spermary cell in mice induced by *m*-nitrobenzene. *Joural of Northeast Normal University*, 37: 115–118.

Yamagishi T, Miyazaki T, 1981. Identification of musk xylene and musk ketone in fresh water fish collected from the tama river Tokyo. *Bulletin of Environmental Contamination and Toxicology*, 26(10): 656–662.

Yurawecz M P, Purna B J, 1983. Nitro musks fragrances as potential contaminants in pesticide reside analysis. *J Assoc Off Anal Chem*, 66(4): 241–247.

Zhang G, Parker A, House A, Mai B, Li X, Kang Y, Wang Z, 2002. Sedimentary records of DDT and HCH in the Pearl River delta, South China. *Environ Sci Technol*, 36: 3671–3677.

Zhang Z L, Hong H S, Zhou J L, 2002. Transport and fate of organochlorine pesticides in River Wuchuan, Southeast China. *J Environ Monitor*, 4: 435–441.

Zhou J L, Hong H S, Zhang Z L, 2002. Multi-phase distribution of organic micropollutants in Xiamen Harbour, China. *Water Res*, 34: 2132–2150.