Bull Environ Contam Toxicol (2009) 82:405–409
DOI 10.1007/s00128-008-9497-3

Preliminary Risk Assessment of Trace Metal Pollution in Surface Water from Yangtze River in Nanjing Section, China

B. Wu · D. Y. Zhao · H. Y. Jia · Y. Zhang · X. X. Zhang · S. P. Cheng

Received: 2 July 2007 / Accepted: 11 July 2008 / Published online: 23 January 2009

Abstract In order to investigate the contamination levels of trace metals, surface water samples were collected from six regions along Yangtze River in Nanjing Section. The concentrations of trace metals (As, B, Ba, Be, Cd, Cr, Cu, Fe, Pb, Li, Mn, Mo, Ni, Sb, Se, Sn, Sr, V and Zn) were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Total concentrations of the metals in the water samples ranged from 825.1 to 950.4 μg/L. The result was compared with international water quality guidelines. Seven metals levels were above the permissible limit as prescribed by guidelines. A preliminary risk assessment was then carried out to determine the human health risk via calculating Hazard Quotient and carcinogenic risk of the metals. Hazard Quotients of all metals were lower than unity, except As. The carcinogenic risk of As and Cd was higher than 10^{-6}, suggesting that those two metals have potential adverse effects on local residents.

Keywords Risk assessment · Trace metal · Yangtze River

Trace metal pollutants in aqueous system can hardly be eliminated and are often recycled via physiochemical and biological processes, which continue to pose a risk of adverse effects on human health and aqueous ecosystem (Ip et al. 2007). Therefore, researchers worldwide focus their attention on quantitative investigation of the trace metals in aquatic ecosystem (Woitke et al. 2003; Olivares-Rieumont et al. 2005; Farkas et al. 2007).

Yangtze River Delta, located in the lower reaches of Yangtze River (Changjiang River), is one of the fast developing regions of China. However the region is suffering enormous environmental deterioration from industrialization. Recently, most investigations of pollutants in Yangtze River have been centered on the specific organic compounds such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorine pesticides (Xu et al. 2001; Liu et al. 2003, 2004; Shen et al. 2006). Only a few reports about trace metals in the Yangtze River are available, mostly on special matrix such as the estuarine sediments (Jing 1999; Chen et al. 2004; Feng et al. 2004; Koshikawa et al. 2007). However, these studies mainly surveyed the levels of metals and possible sources, and did not provide any human health risk assessment by metals. To our best knowledge, there is no reported information about the levels of trace metals in surface water from Yangtze River in Nanjing section and their human risk assessment.

In this study we sampled the surface water from six regions of Yangtze River in Nanjing section and analyzed the levels of nineteen metals. Then the Hazard Quotients (HQs) and carcinogenic risk to human health associated with corresponding metals were assessed via risk assessment model. The approach might provide a reference for future studies.

Materials and Methods

The surface water samples for metal analysis were collected from six regions of the Yangtze River (Fig. 1) in

B. Wu · D. Y. Zhao · H. Y. Jia · Y. Zhang ·
X. X. Zhang · S. P. Cheng (✉)
State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, People's Republic of China
e-mail: chengsp@nju.edu.cn

B. Wu
e-mail: wubingnju@yahoo.com.cn

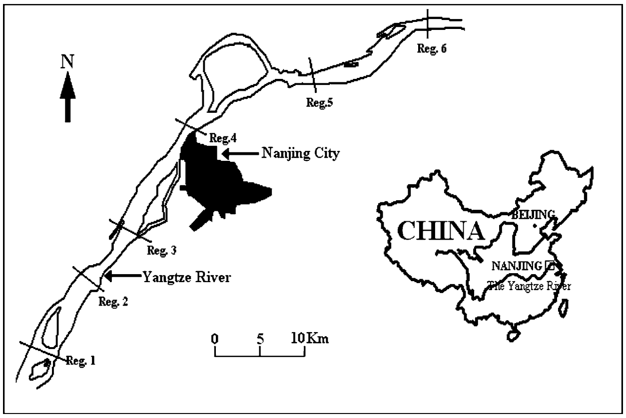

Fig. 1 Location of sampling sites along Yangtze River, Nanjing section. Reg. 1, 2, 3, 4, 5 and 6 represent sampling sites at Jiangninghe, Shangxinhe, Chengnan, Pukou, Xixia and Sanjiangkou, respectively

January 2007. The studied area spreads between 118° and 119° in east longitude and 31° and 32° in north latitude. The samples were collected in precleaned polyethylene bottles. After acidification with HCl, the samples were put in an ice bath, then transported to the laboratory and kept at −20°C until analysis. The mean temperature and pH of water samples were 8.9 and 7.93°C, respectively. The mean electrical conductivity was 230 μS/cm.

The method of State Environmental Protection Administration of China (2002) was used to digest and analyze the water samples. Water samples were measured with inductively coupled plasma-atomic emission spectrometry (ICP-AES, Jarrell-Ash 1100) except for As which was measured by Atomic fluorescence Spectrophotometer (AFS, AF-610A). The elements analyzed included As, B, Ba, Be, Cd, Cr, Cu, Fe, Pb, Li, Mn, Mo, Ni, Sb, Se, Sn, Sr, V and Zn. The detection limit of the measurements was defined as the concentration value which numerically equals to the three times the standard deviation of 10 replicate blank measurements (Pekey et al. 2004). The data is shown in Table 1. The recoveries of the elements ranged from 90% to 110%.

Table 1 Summary statistics of the analytical results of trace metals in water samples from Yangtze River (μg/L)

Elements	Limit of detection	Range	Mean	SD
Arsenic (As)	3.6	7.6–20.8	13.2	4.38
Boron (B)	5	28.4–55.6	37.2	7.9
Barium (Ba)	3	32.9–41.3	37.4	2. 5
Beryllium (Be)	0.2	0.4–1.4	0.5	0.3
Cadmium (Cd)	1	3.2–6.4	4.7	0.91
Chromium (Cr)	4	17.2–24.3	20.9	2.1
Copper (Cu)	4	8.6–12.3	10.7	1.2
Iron (Fe)	10	174.5–350.5	239.8	56.1
Lead (Pb)	30	44–734	55.1	8.6
Lithium (Li)	5	13.1–15.6	14.1	0.8
Manganese (Mn)	1	4.3–8.8	5.4	1. 6
Molybdenum (Mo)	5	6–19.8	11.7	3.9
Nickel (Ni)	5	5.6–24.3	13.4	4.9
Antimony (Sb)	20	49.5–86.9	65.3	11.6
Selenium (Se)	5	5.6–170.7	114.3	46.3
Tin (Sn)	10	58.5–117.8	91.1	17.7
Strontium (Sr)	1	191.1–215.8	210.1	6.6
Vanadium (V)	5	9.7–12	10.5	0.7
Zinc (Zn)	5	7.6–11.6	9.4	1.2
Total metals		923.7–1137.9	1047.1	52.3

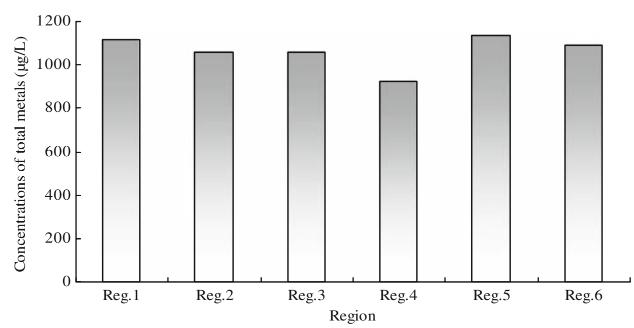

Fig. 2 Total concentrations of nineteen metals in different regions (μg/L)

Results and Discussion

This report presents results from the analysis of nineteen metals in surface water from Yangtze River in Nanjing section, China. The concentration ranges of individual and total metals are shown in Table 1. The total concentrations in surface water ranged from 825.1 μg/L (Reg. 4) to 950.4 μg/L (Reg. 5) with the mean value of 929.29 μg/L (Table 1 and Fig. 2). However, there were no significant differences among the total concentrations in different regions.

In terms of individual metal composition in surface water, all metals were detectable at every site. It was found that Fe was the highest, followed by Sr and As (Table 1). These three metals accounted for 48%–60% of the total concentrations. Levels of seven metals were above the permissible limit as prescribed by US EPA (2003) and WHO (2006), which were As, Cd, Mo, Ni, Pb, Sb and Se.

Three main pathways may occur when target analytes expose to human being: (a) direct ingestion, (b) inhalation through the mouth and nose, and (c) dermal absorption. For metals in water environment, ingestion and dermal absorption play the most important role (Kim et al. 2004). Considering the two pathways mentioned above, the expose dose is calculated using Eqs. 1–2 adapted from the

US Environmental Protection Agency (US EPA 1989; De Miguel et al. 2007):

$$CD_{Iingestion} = \frac{C_w \times IR \times ABS_g \times EF \times ED}{BW \times AT} \quad (1)$$

$$CD_{Idermal} = \frac{C_w \times SA \times K_p \times ABS_d \times ET \times EF \times ED \times CF}{BW \times AT} \quad (2)$$

CDI: exposure dose contacted through ingestion of water ($CDI_{ingestion}$) and dermal absorption (CDI_{dermal}), μg/kg/day; C_w: average concentration of trace metal in water, μg/L; IR: ingestion rate, in this study, 2.2 L/day; SA: exposed skin area, in this study, 2,800 cm^2; K_p: skin adherence factor, cm/h; ABS_g: gastrointestinal absorption factor; ABS_d: dermal absorption factor; ET: exposure time, in this study, 0.6 h/day; EF: exposure frequency, in this study, 365 day/year; ED: exposure duration, in this study, 70 years; CF: unit conversion factor, for water: 1 L/1,000 cm^3; BW: average body weight, in this study, 60 kg; AT: averaging time, for non-carcinogens and carcinogens, 25,550 days; The human health risk assessment was performed by calculating the Hazard Quotients for metals and carcinogenic risk of As and Cd using Eqs. 3–4.

$$\text{Hazard Quotient} = \text{CDI/RfD} \quad (3)$$

$$\text{Carcinogenic Risk} = 1 - \exp(-\text{CDI} \times \text{SF}) \quad (4)$$

RfD is the reference dose for different analytes, expressed in μg/kg/day, which is based on USA. Risk-based concentration table (US EPA 2006), except Pb, which is derived from the World Health Organization's Guidelines (2006). SF is the slope factor of a carcinogen, expressed in $(\mu g/kg/day)^{-1}$, which is based on USA. Risk-based concentration table (US EPA 2006). Toxicity values for dermal absorption have been calculated: oral reference doses are multiplied, and slope factors divided, by an ABS_g to yield the corresponding dermal values (De Miguel et al. 2007).

The Hazard Quotients (HQs) estimated for local residents were summarized in Table 2 based on the oral consumption and dermal absorption of water. The $HQ_{ingestion}$ (hazard quotient of ingestion exposure) of all analytes were smaller than unity, suggesting that these pollutants could pose minimum hazard to local residents. However, $HQ_{ingestion}$ of As was near unity, suggesting that As may be of the serious health concerns for the residents of Nanjing city. The HQ_{dermal} (hazard quotient of dermal absorption) were all below unity, even lower than the $HQ_{ingestion}$, which indicates that the concentrations of these metals may pose little or no health threat via dermal adsorption.

Carcinogenic risk is defined as the incremental probability that an individual will develop cancer during ones lifetime due to chemical exposure under specific scenarios (Chen and Liao 2006; Obiri et al. 2006). For residents of Nanjing, the carcinogenic risk of As and Cd by ingestion and dermal exposure was calculated (Table 3). The risks of Cd ranged from 7.13×10^{-6} to 1.01×10^{-5}. However, the risk of As was three order higher than that of Cd. Under

Table 2 Reference dose and Hazard Quotient for each element

Element	$RfD_{ingestion}$ (μg/kg/day)	RfD_{dermal} (μg/kg/day)	$HQ_{ingestion}$	HQ_{dermal}	$\sum HQ_s$
As	0.3	0.123	0.61	8.45×10^{-5}	0.62
B	200	180	5.70×10^{-3}	5.41×10^{-9}	5.70×10^{-3}
Ba	70	14	4.15×10^{-4}	6.48×10^{-8}	4.16×10^{-4}
Be	2	1	3.58×10^{-3}	1.09×10^{-8}	3.58×10^{-3}
Cd	0.5	0.005	2.85×10^{-3}	2.18×10^{-5}	2.88×10^{-3}
Cr	3	0.015	1.09×10^{-3}	3.34×10^{-5}	1.13×10^{-3}
Cu	40	12	2.42×10^{-3}	2.06×10^{-8}	2.42×10^{-3}
Fe	300	45	3.65×10^{-3}	2.48×10^{-7}	3.65×10^{-3}
Pb	1.4	0.42	3.61×10^{-1}	3.06×10^{-6}	3.61×10^{-1}
Li	20	10	1.09×10^{-2}	3.35×10^{-8}	1.10×10^{-2}
Mn	20	0.8	3.23×10^{-4}	1.54×10^{-7}	3.23×10^{-4}
Mo	5	1.9	2.89×10^{-2}	1.53×10^{-7}	2.89×10^{-2}
Ni	20	5.4	6.35×10^{-3}	1.33×10^{-8}	6.35×10^{-3}
Sb	0.4	0.008	1.03×10^{-1}	1.97×10^{-4}	1.04×10^{-1}
Se	5	2.2	3.12×10^{-1}	1.23×10^{-6}	3.12×10^{-1}
Sn	600	60	4.66×10^{-4}	3.56×10^{-8}	4.66×10^{-4}
Sr	600	120	2.22×10^{-3}	4.23×10^{-8}	2.22×10^{-3}
V	1	0.01	3.30×10^{-3}	2.52×10^{-5}	3.33×10^{-3}
Zn	300	60	1.93×10^{-4}	2.21×10^{-9}	1.93×10^{-4}

Table 3 Carcinogenic risk of As and Cd in different regions

Element	Reg. 1	Reg. 2	Reg. 3	Reg. 4	Reg. 5	Reg. 6
As	3.28×10^{-4}	2.05×10^{-4}	3.10×10^{-4}	2.47×10^{-4}	3.04×10^{-4}	2.82×10^{-4}
Cd	1.01×10^{-5}	9.50×10^{-6}	7.92×10^{-6}	7.13×10^{-6}	9.51×10^{-6}	9.83×10^{-6}

most regulatory program, carcinogenic risk between 10^{-6} and 10^{-4} suggests potential risk (Chen and Liao 2006; Liao and Chiang 2006). The results in this study suggest that the As and Cd in Yangtze River pose potential health risk to the residents.

The results demonstrated that As was the most important pollutant in the Yangtze River of Nanjing section. The As has been proved to cause potentially carcinogenic effects in animals such as the cancers of lung, liver, bladder and skin (Avani and Rao 2007; Bhattacharya et al. 2007), and other effects including hypertension, diabetes and the disorders of nervous system. Therefore, concerted efforts are required to ensure safety of consumers and sustainable development of aqueous ecosystem by removal of As.

It is noteworthy that the approaches employed in this study contain some possible uncertainties. The RfD and SF obtained from US EPA and WHO might not be specific to Chinese (Wei et al. 2006). The distribution of dissolved and particulate elements in water samples was not analyzed. The average concentration of each metal was applied to evaluate the risk level for local residents. Differences in age and exposure conditions might also contribute to different risk. In addition, the effects of contaminants might be modified by the interactions with physiochemical processes. Therefore, this study only presents a preliminary result, and a more precise assessment for trace metals should be carried out in subsequent investigations to evaluate the risk levels and recommend the threshold guideline value for the local government.

Acknowledgement This research was financially supported by the Nanjing University Innovative Foundation (2006071009) and the International Foundation for Science (W/4215-1).

References

Avani G, Rao MV (2007) Genotoxic effects in human lymphocytes exposed to arsenic and vitamin A. Toxicol Vitro 21:626–631. doi:10.1016/j.tiv.2006.12.010

Bhattacharya P, Welch AH, Stollenwerk KG, McLaughlin MJ, Bundschuh J, Panaullah G (2007) Arsenic in the environment: biology and chemistry. Sci Total Environ 379:109–120. doi: 10.1016/j.scitotenv.2007.02.037

Chen SC, Liao CM (2006) Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. Sci Total Environ 366:112–123. doi:10.1016/j.scitotenv.2005.08.047

Chen ZY, Saito Y, Kanai Y, Wei TY, Li LQ, Yao HS, Wang ZH (2004) Low concentration of heavy metals in the Yangtze estuarine sediments, China: a diluting setting. Estuar Coast Shelf Sci 60:91–100. doi:10.1016/j.ecss.2003.11.021

De Miguel E, Iribarren I, Chacon E, Ordonez A, Charlesworth S (2007) Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere 66:505–513. doi:10.1016/j.chemosphere.2006.05.065

Farkas A, Erratico C, Vigano L (2007) Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. Chemosphere 68:761–768. doi:10.1016/j.chemosphere.2006.12.099

Feng H, Han XF, Zhang WG, Yu LZ (2004) A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. Mar Pollut Bull 49:910–915. doi:10.1016/j.marpolbul.2004.06.014

Ip CCM, Li XD, Zhang G, Wai OWH, Li YS (2007) Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. Environ Pollut 147:311–323. doi:10.1016/j.envpol.2006.06.028

Jing Z (1999) Heavy metal compositions of suspended sediments in the Changjiang (Yangtze River) estuary: significance of riverine transport to the ocean. Continent Shelf Res 19:1521–1543. doi: 10.1016/S0278-4343(99)00029-1

Kim EY, Little JC, Chiu N (2004) Estimating exposure to chemical contaminants in drinking water. Environ Sci Technol 38:1799–1806. doi:10.1021/es026300t

Koshikawa MK, Takamatsu T, Takada J, Zhu MY, Xu BH, Chen ZY, Murakami S, Xu KQ, Watanabe M (2007) Distributions of dissolved and particulate elements in the Yangtze estuary in 1997–2002: background data before the closure of the Three Gorges Dam. Estuar Coast Shelf Sci 71:26–36. doi:10.1016/j.ecss.2006.08.010

Liao CM, Chiang KC (2006) Probabilistic risk assessment for personal exposure to carcinogenic polycyclic aromatic hydrocarbons in Taiwanese temples. Chemosphere 63:1610–1619. doi: 10.1016/j.chemosphere.2005.08.051

Liu M, Yang Y, Hou L, Xu S, Ou D, Zhang B, Liu Q (2003) Chlorinated organic contaminants in surface sediments from the Yangtze Estuary and nearby coastal areas, China. Mar Environ Res 46:672–676

Liu M, Yang Y, Xu S, Hou L, Liu Q, Ou D, Jiang H (2004) Persistent organic pollutants (POP_S) in intertidal surface sediments from the Yangtze Estuarine and coastal areas, China. J Coastal Res 43:162–170

Obiri S, Dodoo DK, Okai-Sam F, Essumang DK (2006) Cancer health risk assessment of exposure to arsenic by workers of AngloGold Ashanti–Obuasi Gold Mine. Bul Environ Contam Toxicol 76:195–201. doi:10.1007/s00128-006-0907-0

Olivares-Rieumont S, de la Rosa D, Lima L, Graham DW, D' Alessandro K, Borroto J, Martinez F, Sanchez J (2005) Assessment of heavy metal levels in Almendares River sediments - Havana City, Cuba. Water Res 39:3945–3953. doi:10.1016/j.watres.2005.07.011

Pekey H, Karakas D, Bakoglu M (2004) Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses. Mar Pollut Bull 49:809–818. doi:10.1016/j.marpolbul.2004.06.029

State Environmental Protection Administration of China (2002) Monitoring and analysis method of water and waster water, 4th edn. China Environmental Science Press, Beijing

Shen M, Yu YJ, Zheng GJ, Yu HX, Lam PKS, Feng JF, Wei ZB (2006) Polychlorinated biphenyls and polybrominated diphenyl ethers in surface sediments from the Yangtze River Delta. Mar Pollut Bull 50:1299–1304. doi:10.1016/j.marpolbul.2006.05.023

US EPA (US Environmental Protection Agency) (1989) Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A)

US EPA (2003) National Primary Drinking Water Regulations. http://www.epa.gov/safewater. EPA, office of water

US EPA (2006) Risk-based concentration table. http://www.epa.gov/reg3hwmd/risk/human/rbc/rbc1006.pdf

Wei S, Lau RKF, Fung CN, Zheng GJ, Lam JCW, Connell DW, Fang Z, Richardson BJ, Lam PKS (2006) Trace organic contamination in biota collected from the Pearl River Estuary, China: A preliminary risk assessment. Mar Pollut Bull 52:1682–1694. doi:10.1016/j.marpolbul.2006.06.009

WHO (2006) Guidelines for drinking water quality, 3rd edn. Incorporating first addendum. Recommendations, vol. I, WHO, Geneva

Woitke P, Wellmitz J, Helm D, Kube P, Lepom P, Litheraty P (2003) Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. Chemosphere 51:633–642. doi:10.1016/S0045-6535(03)00217-0

Xu SY, Gao XJ, Liu M, Chen ZL (2001) China's Yangtze estuary II. Phosphorus and polycyclic aromatic hydrocarbons in tidal flat sediments. Geomorphology 41:207–217. doi:10.1016/S0169-555X(01)00117-9