Original Research

Non-Carcinogenic Risks Induced by Heavy Metals in Water from a Chinese River

Ning Liu[1]*, Qin-Yuan Zhu[1], Xin Qian[1], Li Yang[2], Ming-Zhong Dai[1], Xiao-Qing Jiang[1], Na Li[1], Liu Sun[1], Zhi-Chao Liu[1], Gen-Fa Lu[1]

[1]State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing 210046, China
[2]Nanjing College for Population Program Management, Nanjing 210008, China

Received: 9 June 2011
Accepted: 20 January 2012

Abstract

Our study assessed the non-carcinogenic risks of heavy metals in the sources of drinking water treatment plants located along Huaihe River in Jiangsu Province, China. High-resolution inductively coupled plasma-mass spectrometry and inductively coupled plasma-atomic emission spectroscopy were used to determine the levels of eight metals in the water from 30 treatment plants. Non-carcinogenic risks induced by the metals were assessed using the methods recommended by the Environmental Protection Agency of the United States. Among the metals, Fe had the highest concentration and Pb contributed most to the average hazard index (HI) of 30 TWTPs. Except Pb, each metal had an average concentration below the permissible limit of China and the United States. The induced non-carcinogenic risks showed temporal and spatial variations. This study revealed that the metals in the tap water induced negligible public health risks for local residents.

Keywords: drinking water, health risk assessment, heavy metal, river water

Introduction

Jiangsu Province in eastern China is one of the most developed economic regions of China. The Huaihe River is the main source of drinking water for the local residents of North Jiangsu. However, rapid economic growth has led to environmental pollution and ecological damage in this province [1]. Various pollutants, including heavy metals, have been detected in the surface water of the Huaihe [2, 3]. These pollutants, with high toxicities even at trace levels, may pose a potential health risk on the water-consuming population [4, 5]. Few studies have been conducted to investigate the level of metals in Huaihe surface water, but previous reports have indicated that urbanization, industrialization [6], and extensive use of fertilizers on farmlands [3] during the past several decades has led to a rapid increase of the contents of heavy metals in the sediments.

A non-carcinogenic risk assessment model recommended by the Environmental Protection Agency (EPA) of the United States is generally accepted for health risk assessment. This model has been widely used to assess the potential risks induced by the metals in various environments, e.g. Cr, Fe, Mn, Zn, Cd, Pb, and Hg in rivers of China [7]; As, Cd, Pb, and Se in contaminated groundwater in the USA [8]; As in drinking water in Arizona, USA [9]; and Pb and Mn in the Nakivubo Stream water in Uganda [10, 11]. Currently, concerns mainly focus upon the quantitative detection of heavy metals in Huaihe water and sediments [2, 3]. However, information is limited about the health risks posed by the metals in the source of drinking water in China. This study aimed to carry out a preliminary assessment on non-carcinogenic risks induced by the metals of Cr, Fe, Mn, Zn, Cd, Pb, Hg, and Cu in the sources of 30 water treatment plants (TWTPs) in Jiangsu Province, China, based on chemical detections during 2007-10.

*e-mail: liuning1991@gmail.com

Materials and Method

Water Sampling

Source water samples were collected from a total of 30 TWTPs located along the Huaihe River (33º53.4'N, 118º12.6'E-32º37.2'N, 119º28.2'E) at the section of Jiangsu Province of China (Fig. 1). Source water (1 L) was sampled once every 3 months from February 2007 to August 2010, and each sampling was performed in triplicate. The water samples were acidified with 37% HCl (for Fe) or 0.2% HNO_3 (for other metals) to reach pH<2 before being transported to the laboratory, and then stored at 4ºC until analysis.

Measurement of Heavy Metals in Water

Before storage, water samples (10 ml each) were filtered through a cellulose acetate membrane filter (0.2-μm pore size). Dissolved trace elements, including Cr, Fe, Mn, Zn, Cd, Pb, Hg, and Cu were analyzed using high-resolution inductively coupled plasma-mass spectrometry (HRICP-MS; Agilent 7500, USA) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Jarrell-Ash 1100, USA). In order to make results reliable, the accuracy of the measurements was assured by cross-evaluation between different methods, e.g. ICP-AES versus HRICP-MS. The results of cross-checking agreed within ±5%. Calibration curves had R^2 of over 0.999 and standard deviations (SD) of triplicates were below 5%. The detection limits were 0.002 $\mu g \cdot L^{-1}$ for Cr, Fe, Hg, Mn, and Pb; 0.005 $\mu g \cdot L^{-1}$ for Cd and Cu; and 0.01 $\mu g \cdot L^{-1}$ for Zn.

Non-Carcinogenic Risk Assessment

Based on the determination of metal concentration, non-carcinogenic risk assessment was carried out according to the reliable exposure pathways of contaminants recommended by USEPA [12, 13]. The potential exposure pathways of the metals included:

(1) direct ingestion of water consumption

(2) dermal absorption of contaminants in water adhered to exposed skin.

According to the EPA [12], exposure doses via ingestion and dermal absorption were calculated by Eqs. 1 and 2, respectively:

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

$$D_d = \frac{C_w \times SA \times Kp \times ET \times EF \times ED \times CF}{BW \times AT} \quad (2)$$

...where D_i ($\mu g \cdot kg^{-1} \cdot day^{-1}$) is the exposure dose through ingestion of water, D_d ($\mu g \cdot kg^{-1} \cdot day^{-1}$) is the exposure dose through dermal absorption, and Cw ($\mu g \cdot L^{-1}$) is the concentration of metals in drinking water. Other parameters and their values applied in this study are listed in Table 1.

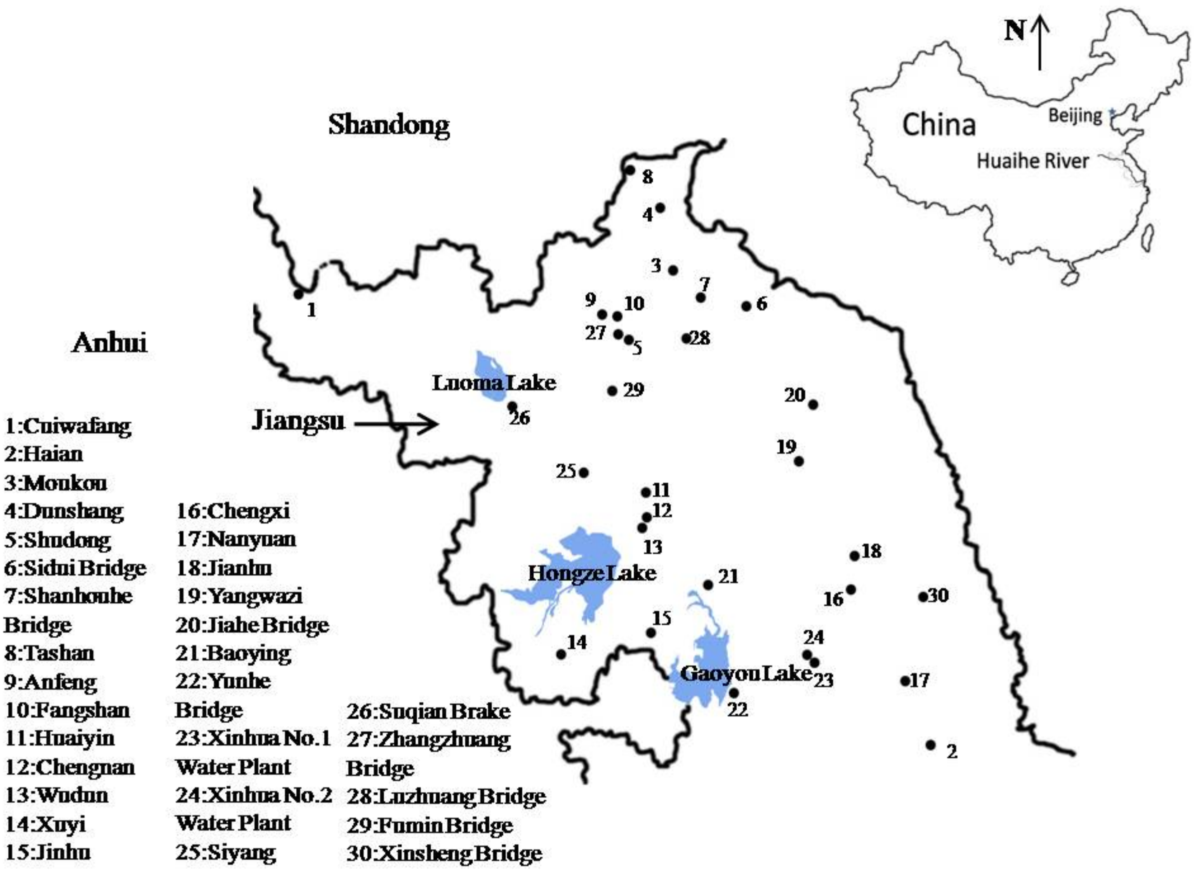

Fig. 1. Source water sampling locations of 30 drinking water treatment plants along the Huaihe River, China.

Table 1. Parameters and values recommended by the U.S. EPA for the assessments on non-carcinogenic risks of the metals.

Parameters	Descriptions	Values
AT, day	Average time	25,550
BD, kg	Body weight	60
CF, L·cm^{-3}	Unit conversion factor	1/1,000
ED, year	Exposure duration	70
EF, day·year^{-1}	Exposure frequency	365
ET, h·day^{-1}	Exposure time during bathing and shower	0.6
IR, L·day^{-1}	Ingestion rate	2.2
Kp, cm·h^{-1}	Dermal permeability coefficient	0.2
SA, cm^{2}	Exposed skin area	2,8

The hazard quotient (*HQ*) was calculated by Eq. 3 to estimate non-carcinogenic risk [12]:

$$HQ = \frac{D}{RfD} \quad (3)$$

...where *D* (μg·kg^{-1}·day^{-1}) is the exposure dose obtained from Eqs. 1 and 2 and *RfD* (μg·kg^{-1}·day^{-1}) is the reference dose of the contaminant. The values of ingestion reference dose (RfD_i) were obtained from the EPA [14]. RfD_i was multiplied by a gastrointestinal absorption factor to yield the corresponding dermal absorption reference dose, RfD_d [12].

According to Eq. 4 [12], the sum of individual *HQ* of each metal, expressed as the hazard index (*HI*), was used to assess the overall non-carcinogenic risk posed by all the metals in one TWTP.

$$HI = \sum_{i=1}^{n} HQi \quad (4)$$

Statistical Analysis

Experimental results were statistically analyzed using Excel 2007 (Microsoft Excel, Washington, USA). All values were expressed as the mean ±SD. The significance of the difference among the concentrations of the metals in different TWTPs was assessed with independent samples *t* test. A $p<0.05$ was considered statistically significant.

Results and Discussion

Concentration of Metals in Source Waters

This study investigated the concentrations of eight metals in water at sources for 30 sample sites (TWTPs) in Jiangsu Province, China, 2007-10 (Fig. 2). Average concentrations of Cr, Fe, Mn, Cu, Zn, Cd, Pb, and Hg in the 30 TWTPs were 4.02, 107.7, 19.6, 10.2, 19.6, 0.823, 4.5, and 0.027 μg·L^{-1}, respectively (Fig. 2). Our previous study also indicated that Fe among the metals had the highest concentration in the water of Yangtze River and Taihu Lake (China), while Zn had higher level than other metals in the groundwater of the Huaihe River Basin [1].

Cd had higher contamination levels than Zn and Cu in the mainstream at the Wuhan Section of the Yangtze River [15]. The level of each metal determined in this study was below the maximum permissible limit of China [16], but the concentration of Pb in most of the sampling sites exceeded the maximum permissible limit as set by the EPA [14]. The health risk problem has potentially arisen with lead pollution recorded in water and sediments of the Huaihe River Basin [17].

Non-Carcinogenic risk Induced by the Metals

A preliminary non-carcinogenic risk assessment was carried out for the metals in water at source for the 30 sampling sites based on the results of chemical detections. Fig. 3 summarizes *HQ* of each metal according to the oral consumption (*HQi*) and dermal absorption (*HQd*) of water. Both *HQs* (the sum of *HQi* and *HQd*) of the individual metals and HI (total non-carcinogenic risk) of each TWTP were lower than 0.5, the non-carcinogenic *HI* recommended by USEPA [14], demonstrating that these pollutants could pose negligible hazards to public health of local residents.

Among these metals, Pb contributed most (30.8%) to the average *HI* of 30 TWTPs, followed by Cd (25.9%) and Cr (23.8%), demonstrating that the three metals may be of serious health concerns for the local residents. A previous study also showed that Pb in the groundwater of North Jiangsu contributed most to the non-carcinogenic risks induced by several metals [1]. However, Wu et al. indicated that As and Cd in the Yangtze induced the highest health risks compared to the other 16 metals [18]. Cr enrichment in the sediments of the Huaihe was widespread [2], and the sequence of the potential ecological risk posed by the metals in Yangtze sediments at the Wanzhou Section was Cd > Pb > Cu > Zn > Cr [4]. These metals can be easily bio-accumulated in some fish species [19, 20], so more concerns should focus on the contamination by Pb, Cd, and Cr in the source water of Huaihe River.

Temporal and Spatial Variations of *HIs*

Concentrations of the metals in water samples showed temporal and spatial variations (Fig. 2). The average concentration of Cr in the source water at Fumin Bridge was 36.5 μg·L^{-1} in 2007 and decreased to 7.7 μg·L^{-1} in 2009, but the concentration was around 3.3 μg·L^{-1} in most of the other sites during 2007-10 (Fig. 2a). Meanwhile, the average concentration of Cd in the water sampled from Fumin Bridge was 3.0 μg·L^{-1} in 2008, and increased to 6.7 μg·L^{-1} in 2009, while the concentration was around 0.8 μg·L^{-1} in most of the other sites during 2007-10 (Fig. 2f). The average *HIs* of Huaihe River were 0.26±0.17. Comparison of HIs among the 30 sampling sites showed that the three sites at

Luzhuang Bridge (28), Fumin Bridge (29), and Xinsheng Bridge (30) had higher *HIs* than other sampling sites, while Maokou (3) had a relatively lower *HI* (Fig. 3). Source water of the three sites were collected from Gupo River or Caimi River, which are Huaihe River branches and have been heavily polluted because they are located near the Chemical Industrial Park of Lianyungang City (Jiangsu Province). Several big companies in the industrial area are engaged in ink production, or printing and dyeing processing, which may be responsible for the heavy metal pollution.

Since the three TWTPs (28-30) are heavily polluted, we further investigated the seasonal changes of *HIs* of the sites. Lower *HIs* always occurred in summer (August) compared with other seasons (Fig. 4). It is self-evident that metal pollutants are more easily concentrated in the low-flow periods [21], resulting in the noteworthy temporal fluctuations of *HIs*. A previous study also revealed the seasonal variations in river water quality with respect to heavy metal contamination [22]. However, Aktar et al. found that the concentration of various metals in the surface water of the Ganges River in India were higher in the rainy season and lower in the winter season [23]. Li et al showed that Fe, Mn, and Zn were concentrated significantly by *Onchidium struma* in summer or autumn, while Cd, Cr, and Pb were more likely to be bio-concentrated in spring and winter [5, 24]. Thus, more concerns should focus on seasonal variations of the contents of those metals in surface water and aquatic organisms in the region of the Huaihe River.

Conclusions

Among the metals analyzed, Fe had the highest concentration in water sources during 2007-10. The level of each metal (except Pb) was below the water quality standards required by China and the USA. Both *HQs* of indi-

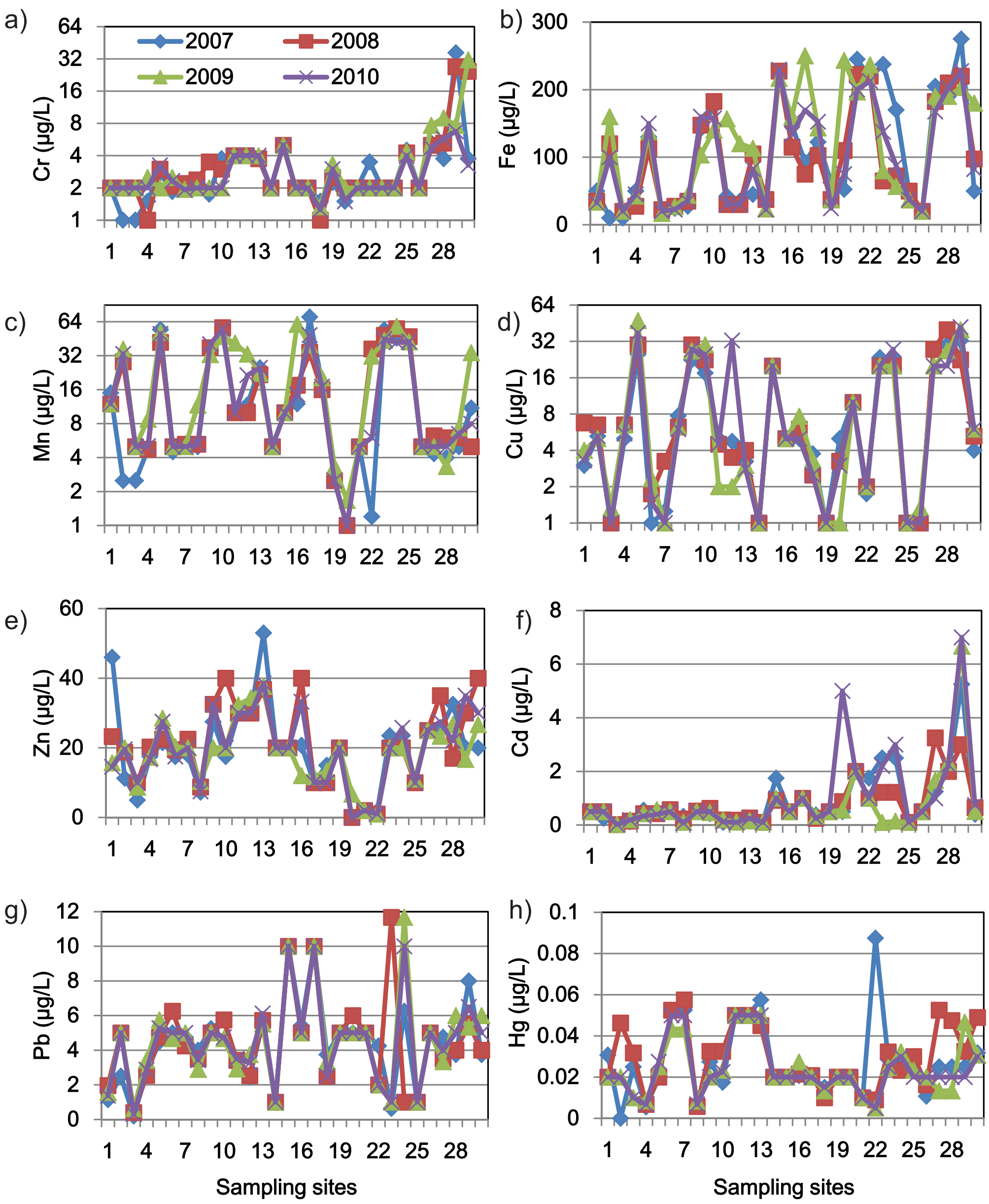

Fig. 2. Concentrations of Cr (a), Fe (b), Mn (c), Cu (d), Zn (e), Cd (f), Pb (g), and Hg (h) in the source water of 30 drinking water treatment plants along the Huaihe River of China.

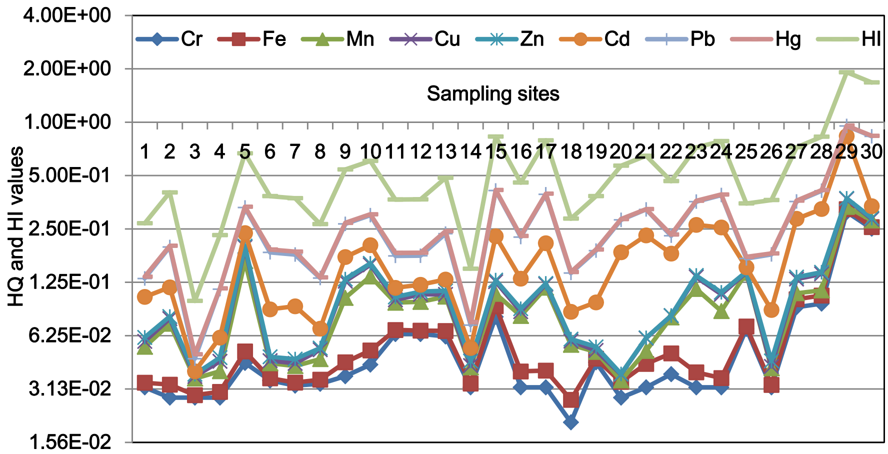

Fig. 3. *HQs* of individual metals and *HI* of each drinking water treatment plant in the Huaihe River. Water sampling at each location of the water treatment plants was performed in triplicate for a total of 11 times from February 2007 to August 2009.

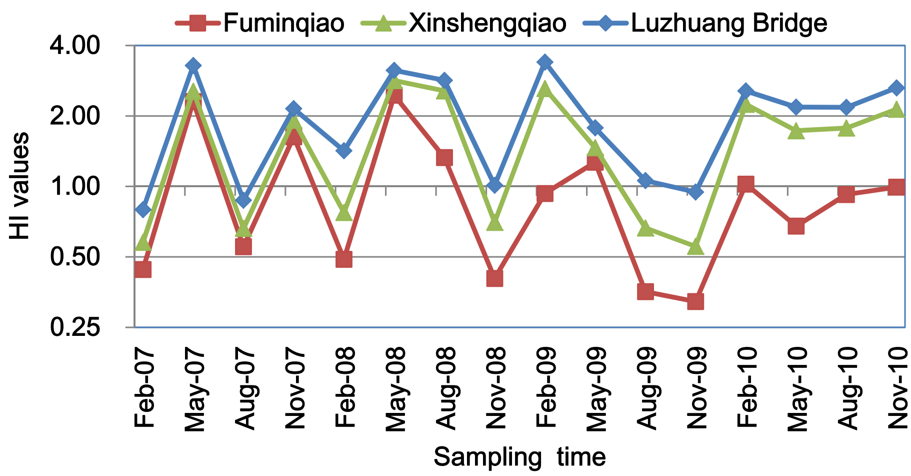

Fig. 4. Temporal variation of *HI* of total non-carcinogenic risk induced by metals in the source water of the three drinking water treatment plants of Fumin Bridge, Xinsheng Bridge, and Jinhu.

vidual metals and *HI* of each TWTP were below non-carcinogenic *HI*. High *HIs* appeared more frequently in low water season. Therefore, an in-depth investigation is needed for the temporal and spatial variations of health risks induced by the contamination of metals in drinking source water of Huaihe River.

Acknowledgements

This study was financially supported by the Science & Technology Foundation for Environmental Protection of Jiangsu Province, China (2008022).

References

1. LIU N., NI T. H., XIA J., DAI M. Z., HE C. Y., LU G. F. Non-carcinogenic risks induced by metals in drinking source water of Jiangsu Province, China. Environ. Monit. Assess., **177**, (1-4), 449, **2011**.
2. HUANG H., OU W. H., WANG L. S. Semivolatile organic compounds, organochlorine pesticides and heavy metals in sediments and risk assessment in Huaihe River of China. J. Environ. Sci. **18**, (2), 236, **2006**.
3. ZHANG H., SHAN B. Historical records of heavy metal accumulation in sediments and the relationship with agricultural intensification in the Yangtze-Huaihe region, China. Sci. Total Environ. **399**, (1-3), 113, **2008**.
4. FU C., GUO J. S., PAN J., QI J. S., ZHOU W. S. Potential ecological risk assessment of heavy metal pollution in sediments of the Yangtze River within the Wanzhou Section, China. Biol. Trace Elem. Res. **129**, (1-3), 270, **2009**.
5. LI X. B., JIA L. Z., JIA Y. L., WANG Q., CHENG Y. X. Seasonal bioconcentration of heavy metals in *Onchidium struma* (Gastropoda: Pulmonata) from Chongming Island, the Yangtze Estuary, China. J. Environ. Sci. **21**, (2), 255, **2009**.
6. XUE B., YAO S. C., XIA W. L. Environmental changes in Lake Taihu during the past century as recorded in sediment cores. Hydrobiologia **581**, 117, **2007**.
7. LIU N., XIA J., DAI M. Z., NI T. H., HE C. Y., ZHANG X. X., LU G. F. A preliminary non-carcinogenic risk assess-

ment on metals in source water of the Yangtze River (lower reach). Fresen. Environ. Bull. **19**, (8A), 1648, **2010**.
8. PELOW D., EDMONDS R. Health risks associated with contamination of groundwater by abandoned mines near Twisp in Okanogan County, Washington, USA. Environ. Geochem. Health **26**, 69, **2004**.
9. SOFUOGLU S. C., LEBOWITZ, M. D., O'ROURKE M. K., ROBERTSON G. L., DELLARCO M., MOSCHANDREAS D. J. Exposure and risk estimates for Arizona drinking water. Am. Water Works Assoc. J. **95**, (7), 67, **2003**.
10. SEKABIRA K., ORIGA H. O., BASAMBA T. A., MUTUMBA G., KAKUDIDI E. Assessment of heavy metal pollution in the urban stream sediments and its tributaries. Int. J. Environ. Sci. Tech. **7**, (3), 435, **2010**.
11. SEKABIRA K., ORIGA H. O., BASAMBA T. A., MUTUMBA G., KAKUDIDI E. Heavy metal assessment and water quality values in urban stream and rain water. Int. J. Environ. Sci. Tech. **7**, (4), 759, **2010**.
12. USEPA (U.S. Environmental Protection Agency): Risk assessment guidance for superfund volume I human health evaluation manual. **2011**. http://www.epa.gov/oswer/riskassessment/ragsa/pdf/rags-vol1-pta_complete.pdf. Accessed Mar 5, **2011**.
13. USEPA (U. S. Environmental Protection Agency): Exposure factors handbook. **2011**. http://www.cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=22463. Accessed Mar 5, **2011**.
14. USEPA (U. S. Environmental Protection Agency): Regional Screening Level (RSL) Tapwater Supporting Table. http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/index.htm. Accessed Nov 6, **2011**.
15. YANG Z. F., WANG Y., SHEN Z. Y., NIU J. F., TANG Z. W. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. J. Hazard. Mater. **166**, (2-3), 1186, **2009**.
16. SEPAC (State Environmental Protection Administration of China): Monitoring and analysis method of water and wastewater (4th Ed.). China Environmental Science Press. **2002**.
17. YAO S. C., XUE B., XIA W. L., ZHU Y. X., LI S. J. Lead pollution recorded in sediments of three lakes located at the middle and lower Yangtze River Basin, China. Quatern. Int. **208**, 145, **2009**.
18. WU B., ZHANG X. X., ZHANG X. L., YASUN A., ZHANG Y., ZHAO D. Y., FORD T., CHENG S. P. Semi-volatile organic compounds and trace elements in the Yangtze River source of drinking water. Ecotoxicology **18**, 707, **2009**.
19. BRUCKA-JASTRZEBSKA E. The effect of aquatic cadmium and lead pollution on lipid peroxidation and superoxide dismutase activity in freshwater fish. Pol. J. Environ. Stud. **19**, (6), 1139, **2010**.
20. KALISINSKA E., SALICKI W. Lead and cadmium levels in muscle, Liver, and kidney of scaup Aythya marila from Szczecin Lagoon, Poland. Pol. J. Environ. Stud. **19**, (6), 1213, **2010**.
21. MELO C. A., MOREIRA A. B., BISINOTI M. C. Seasonal and spatial trend of pollutants in the waters of the Sao Jose Do Rio Preto municipal dam, Sao Paulo State, Brazil. Quim. Nova. **32**, (6), 1436, **2009**.
22. REZA R., SINGH G. Heavy metal contamination and its indexing approach for river water. Int. J. Environ. Sci. Tech. **7**, (4), 785, **2010**.
23. AKTAR M. W., PARAMASIVAM M., GANGULY M., PURKAIT S., SENGUPTA D. Assessment and occurrence of various heavy metals in surface water of Ganga River around Kolkata: A study for toxicity and ecological impact. Environ. Monit. Assess. **160**, (1-4), 207, **2010**.
24. FAN A. M., HOWD R. Symp XIVd current issues in metal toxicity with specific references to As, Cd, Cr, and Se. Int. J. Toxicol. **30**, (1), 133, **2011**.