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RESEARCH ARTICLE

Spatial distribution, health risk assessment and statistical source identification of the trace elements in surface water from the Xiangjiang River, China

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Abstract Surface water samples were collected from the sampling sites throughout the Xiangjiang River for investigating spatial variation, risk assessment and source identification of the trace elements. The results indicated that the mean concentrations of the elements were under the permissible limits as prescribed by guidelines except arsenic (As). Based on the health risk indexes, the primary contributor to the chronic risks was arsenic (As), which was suggested to be the most important pollutant leading to non-carcinogenic and carcinogenic concerns. Individuals, who depend on surface water from the Xiangjiang River for potable and domestic use, might be subjected to the integrated health risks for exposure to the mixed trace elements. Children were more sensitive to the risks than the adults, and the oral intake was the primary exposure pathway. Besides, multivariate statistical analyses revealed that arsenic (As), cadmium (Cd), lead (Pb), selenium (Se), and mercury (Hg) mainly derived from the chemical industrial wastewaters and the coal burning, and zinc (Zn) copper (Cu) and chromium (Cr) mainly originated from the natural erosion, the mineral exploitation activities, and the non-point agricultural sources. As a whole, the upstream of the Xiangjiang River was explained as the high polluted region relatively.

Keywords Xiangjiang River · Trace element · Human health risk · Source identification · Surface water · Children

Introduction

Surface waters are highly vulnerable to pollutions by the trace elements due to the easy accessibility to the disposal of wastewaters (Zhang et al. 2010a), which has drew worldwide concerns among environmental health researchers. Although some trace elements are essential as micronutrients for normal growth of humans and animals, high intake of them could lead to potential toxicity for the environment and human beings (Goldhaber 2003). Trace elements, especially some of the heavy metals, are non-degradable, persistence, and often recycled via physiochemical and biological processes, which can be accumulated in the human body system, causing significant threats to human health by inducing damage to nervous system and internal organs (Ip et al. 2007; Lee et al. 2007; Lohani et al. 2008). The potential risks of the exposure to trace elements are widely known including infectious diseases, acute or chronic chemical toxicity, and carcinogenicity. Therefore, long-term exposure to trace elements in water could cause adverse effects on human health. The only measurements of water quality are not insufficient. It is essential to translate the observed impacts on water quality into possible human health risks as well as the implications by multiple

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threat exposure pathways. The water quality characteristic (Giri and Singh 2014; Iqbal et al. 2013), the spatial patterns (Li and Zhang 2010; Phan et al. 2013), the hazardous effects, and the potential risks on human health relating to metals and elements (Asante et al. 2007; De Miguel et al. 2007; Zheng et al. 2008) have been reported in previous researches.

Generally, trace elements in surface water from river in urban areas could be derived from natural processes and anthropogenic sources, which lead to the increase in the level of metals and elements concentrations in river water (Banerjee et al. 2012; Mondal et al. 2010; Phan et al. 2010). Natural processes are including erosion, chemical weathering of rocks and soils, wet and dry fallout of atmospheric particulate matter, and microbial mediated reductive dissolution, etc. Anthropogenic sources are including domestic and municipal sewage discharge, industrial wastewater discharge, and agricultural fertilizer leaching, etc. Recently, the surface water in river ecosystem has become increasingly contaminated by the drainage of mixed trace elements (Oberholster 2011), since river basins generally constitute areas with a high population density owing to favorable living conditions and industrial bases. Therefore, it is likely that people inhabiting and traveling around inland watersheds are affected by direct discharge of effluents containing trace elements from various sources in aquatic systems.

The Xiangjiang River, one of the main tributaries of the Yangtze River, is undertook as an important role of supplying drinking water for residents in middle area of China. The Xiangjiang River basin is very well known for its rich fertile soil and abundant mineral resources. Unfortunately, with the rapid industrial and agricultural growth, an increasing amounts of trace elements concentrated wastewaters flow into the Xiangjiang River. The limited capabilities of water treatment on top of careless agricultural, industrial, and municipal sectors lead to a steady decline in the water quality level. The previous researches focused on characterizing the surface water quality and the control pollutants of the surface water (Chen et al. 2004; Sun et al. 2006; Zhang et al. 2010b). However, to our best knowledge, there are few studies available on the systematic and comprehensive investigations about the trace elements in surface water from the Xiangjiang River, involving their spatial characterization, possible source identification, and potential health risks via the multiple pathways.

Considering the facts above, the objectives of this study are to (1) determine spatial distribution of the trace elements in surface water from the Xiangjiang River; (2) assess human health risks with the hazard quotients (HQs) of the individual trace element and the hazard index (HI) of the mixed trace elements through the pathways of ingestion and dermal absorption, respectively; (3) further study the carcinogenic risks from the trace elements; and (4) identify the natural and/or anthropogenic sources of these trace elements employing multivariate statistical techniques.

Materials and methods

Study area

The Xiangjiang River, the main tributary of the Yangtse River, is located in Middle China. It is originated from the Yegaoling Mountain, traverses a distance of 968 km, and its mainstream flows across six cities including Yongzhou, Hengyang, Zhuzhou, Xiangtan, Changsha, and Yueyang before discharging into the Yangtse River through the Dongting Lake (Fig. 1).

The Xiangjiang River basin with an area of 94,721 km^2 maintains a population of 30 million at least and is subjected to the subtropical monsoon climate. Its mainstream serves as the major source for the agricultural irrigation and the domestic and industrial water supply in the Xiangjiang River basin. Since the Three Gorges Dam which is the biggest hydropower project in the world has been established, the velocity of flow in the Xiangjiang River has been reduced, which may have negative impacts on the water quality. Therefore, the assessments of the surface water quality and the human health risk of the Xiangjiang River were quite essential, which have direct and significant effects on regional drinking water safety.

Samples collection

The work was implemented after the research proposal was approved and assisted by Department of the Hydrological Management along the Xiangjiang River. Samples were collected from 15 sampling sites monthly during the year of 2011, which were chose according to the current hydrologic stations along the Xiangjiang River. The designations and locations of the sampling sites in this study were given in Fig. 1. The sites number from 1 to 15 hereafter referred as S1 to S15. In each site, three replicates including the waters near riverbanks and center of the river were collected and well mixed in situ subsequently. Surface water samples were filtered through 0.45 mm pore size filters and collected in preconditioned acid-washed polyethylene containers. After acidification with concentrated nitric acid, the samples were kept in an ice box and then transported and stored into a fridge until analysis in an accredited analytical laboratory. Individual demographic information, such as age and weight, was also collected for the calculation of the average daily dose of each element to the individual in the studied population using a structured questionnaire.

Determination of trace element concentrations

The concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), selenium (Se), zinc (Zn), and mercury (Hg) in surface water samples were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) and atomic fluorescence spectrometry (AFS) under optimum analytical

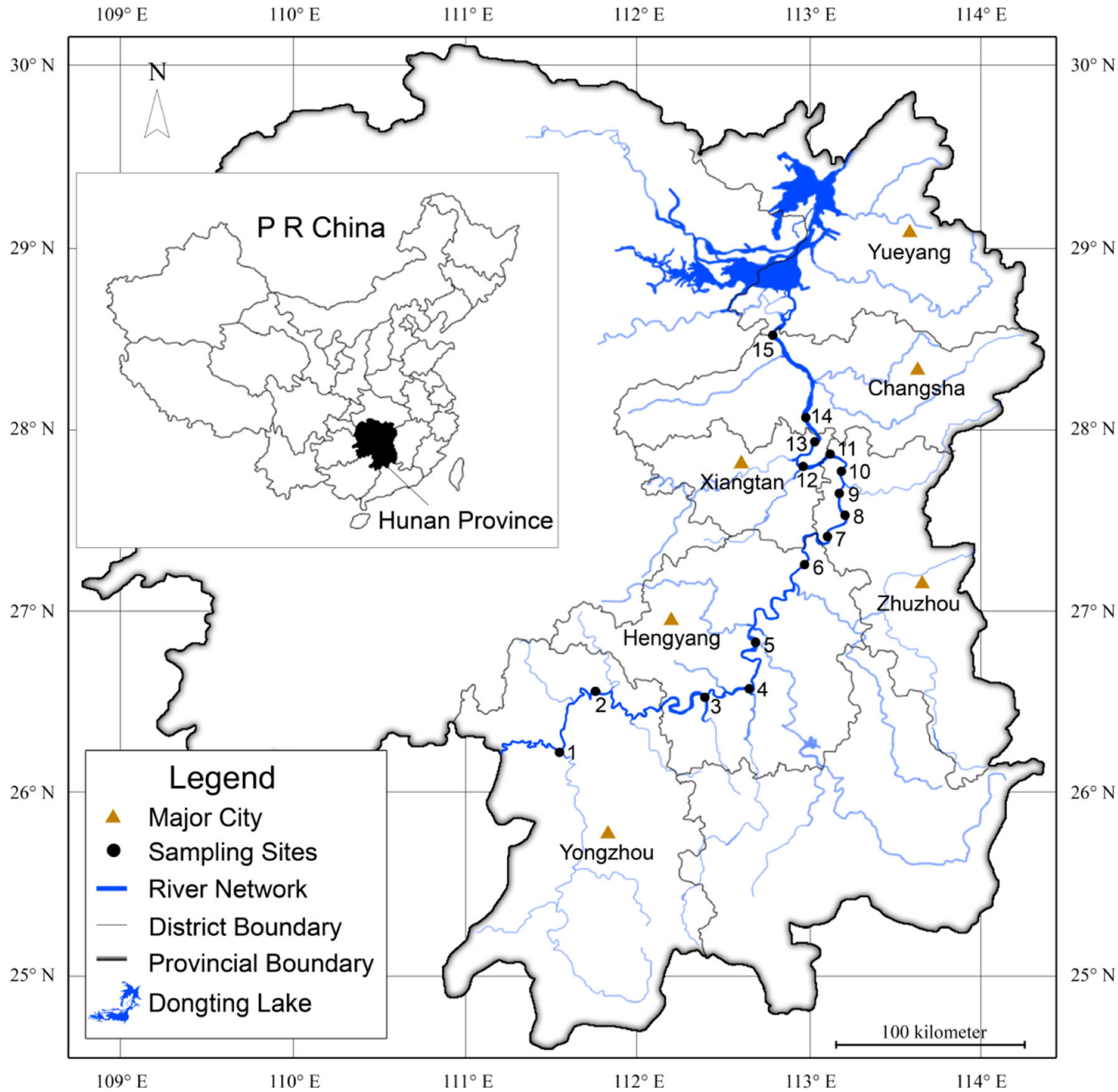

Fig. 1 Map of the sampling site locations along the Xiangjiang River

conditions. The sampling containers were rinsed several times with the fresh surface water before collecting the water samples. Quality assurance and quality control were assessed using duplicates, reagent blanks, and certified reference materials, with each batch of samples. Matrix interference (Blank) was <2 % for all elements. Triplicates of samples analysis yielded relative percent differences of <5 %. Each calibration curve was evaluated by analyses of quality control standards before, during, and after the analyses of a set of samples. When the recovery rate become out of the recommended range (90–110 %), samples were reanalyzed with a new calibration curve.

Health risk assessment

Health risk assessment is defined as the processes of estimating the probability of occurrence of events and the probable magnitude of adverse health effects over a specified time period (Lim et al. 2008). Exposure of human being to trace elements in the water could occur via three main pathways including direct ingestion, inhalation through mouth and nose, and dermal absorption through exposure skin (De Miguel et al. 2007). For trace elements in water environment, ingestion, and dermal absorption play the most important roles (Giri and Singh 2014; Kim et al. 2004). Generally, the ingestion and the dermal absorption of water are expressed by the processes of human daily water drinking and daily showering, respectively. Considering the two pathways mentioned above, the doses received through the individual pathway considered are determined using Eqs. (1) and (2), which are adapted from the risk assessment guidance by United States Environmental Protection Agency (USEPA) (Rodriguez-Proteau and Grant 2005; USEPA 2004). According to the questionnaires, the residents in the basin depend on surface water from the Xiangjiang River for potable and domestic use for the whole year. And local residents are classified into two groups of the children and the adults in this study.

$$CD_{\text{ing}} = \frac{C_{\text{w}} \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

$$CD_{\text{derm}} = \frac{C_{\text{W}} \times SA \times K_{\text{p}} \times ET \times EF \times ED \times 10^{-3}}{BW \times AT} \quad (2)$$

where CD_{ing} (μg/kg/day) and CD_{derm} (μg/kg/day) are the average daily exposure doses contacted through ingestion and dermal absorption of water, respectively; C_w is the average concentration of the studied element in water (μg/L); IR is the ingestion rate of water (L/day), in this study, 1.5 L/day for child and 2.2 L/day for adult; EF is the exposure frequency (day/a), in this study, 350 days/a, for subtracting 15 days per year which were assumed to be spent away from the usual residence; ED is the exposure duration (a), in this study, 6 a for child and 30 a for adult; BW is the body weight (kg), in this study, 22 kg for child and 65 kg for adult; AT is the averaging time (day), in this study, 2190 days for child and 10,950 days for adult; SA is the exposed skin area (cm^2), in this study, 6660 cm^2 for child and 18,000 cm^2 for adult; Kp is the dermal permeability coefficient in water (cm/h), in this study, 0.001 cm/h for As, Cd, Cu Se, and Hg, 0.0001 cm/h for Pb, 0.002 cm/h for Cr, and 0.0006 cm/h for Zn; ET is the exposure time (h/day), in this study, 0.6 h/day. The above exposure variables were based on the results of the questionnaires, the relevant researches, and the standards by United States Environmental Protection Agency (Iqbal et al. 2013; Phan et al. 2013; USEPA 1989, 2004; Wu et al. 2009).

Risk characterization is quantified by carcinogenic risk and non-carcinogenic risk (Li and Zhang 2010). To reflect potential non-carcinogenic risks of trace elements, the hazard quotients (HQs) were estimated by comparing exposure of contaminant from each exposure way with the corresponding reference dose (RfD) using Eqs. (3) and (4). Non-carcinogenic effects are considered if HQ>1. The hazard index (HI) is introduced for evaluating the aggregate non-carcinogenic risks posed by the mixed trace elements from all the applicable pathways using the Eq. (5). While HI greater than 1, it is indicating a potential for adverse effects on human health (Phan et al. 2013).

$$HQ_{\text{ing/derm}} = {}^{CD_{\text{ing/derm}}}/_{RfD_{\text{ing/derm}}} \quad (3)$$

$$RfD_{\text{derm}} = RfD_{\text{ing}} \times ABS_{\text{GI}} \quad (4)$$

$$HI = \sum_{i=1}^{n} \left(HQ_{ing} + HQ_{derm} \right) \quad (5)$$

where $HQ_{\text{ing/derm}}$ is the hazard quotient through ingestion or dermal absorption of water (unitless); HI is the hazard index (unitless), which is the sum of the HQs from all the applicable pathways (the pathways classified into two pathways of the ingestion and the dermal absorption in this study); *i* is the kind of the trace element; RfD is the reference dose of the individual element (μg/kg/day), RfD_{ing} is the oral reference dose which obtained from a database of risk-based concentration table (USEPA 2013) and the World Health Organization's Guidelines (WHO 2008), and RfD_{derm} is the reference dose of the dermal absorption; ABS_{GI} is the gastrointestinal absorption factor, originated from researches by the USEPA (USEPA 2013) and Rodriguez-Proteau and Grant (Rodriguez-Proteau and Grant 2005).

Carcinogenic risk of trace elements was evaluated using Eq. (6) and the detailed calculating process was followed by (Li and Zhang 2010). Carcinogenic risk is defined as the incremental probability that an individual is developing any type of cancer during a lifetime due to chemical exposure under specific scenarios (Chen and Liao 2006; Obiri et al. 2006). Carcinogen risk assessment model has generally been based on the premise that the risk is proportional to cumulative lifetime dose. For lifetime human exposure scenarios, the exposure metric which used for carcinogenic risk assessment is the lifetime average daily dose (the average lifetime is 70 years in this study). These metrics are typically used in conjunction with the corresponding slope factor to calculate individual cancer risk. The acceptable range of carcinogenic risks by the USEPA is 10^{-6} to 10^{-4} (Rodriguez-Proteau and Grant 2005).

$$CR_{\text{i}} = \sum_{n=1}^{\text{j}} \left(CD_{\text{j}} \times CSF \right) \quad (6)$$

where CR is the carcinogenic risk; CD is the average daily exposure doses; CSF is the cancer slope factor of a carcinogen $(\mu g/kg/day)^{-1}$, which is based on risk-based concentration table by the USEPA (De Miguel et al. 2007; USEPA 2013); i is the kind of the trace element; j is the kind of the exposure pathway.

Statistical data analyses

Multivariate analyses of the trace elements concentrations data set are performed using Pearson's correlation analysis, principal component analysis (PCA) techniques, and cluster analysis (CA) by the software package SPSS version 18.0 for Windows.

Correlativity among the selected elements was tested using Pearson's coefficient with statistical significance set at $p<0.05$ (Varol 2011). PCA of the normalized variables in this study was performed to extract significant principal components (PCs) which provided information on the most meaningful parameters and were retained while the eigenvalue >1. Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests were performed to examine the suitability of the data for PCA. Hierarchical agglomerative cluster analysis, which is one of the most common approaches of cluster analysis (CA), was performed on the normalized data set to reveal a system of organizing variables based on their nearness or similarity, using Ward's method with Euclidean distances as a measure of similarity (Varol and Sen 2012).

Results and discussion

Distribution of the trace elements in the surface water

The concentrations of individual and total trace elements are shown in Table 1 and Fig. 2. The total concentrations of the studied trace elements in surface water were observed to range from 32.91 μg/L (S15) to 585.04 μg/L (S2), with the mean value of 132.06 μg/L. It was found that the mean concentration level of Zn (84.57 μg/L) was the highest, followed by that of Cu (20.33 μg/L) and As (12.24 μg/L). These three elements accounted for 88.70 % of the total concentrations. However, the lowest average level was found for Hg (0.04 μg/L). The trace elements showed significant fluctuations in the surface water samples from various sites, especially Cu and Zn which had the larger standard deviation compared to the other elements. Being shown in Fig. 2, S2 (585.04 μg/L) owned the highest total concentrations of the trace elements, followed by S3 (309.51 μg/L) and S4 (227.66 μg/L), and S15 (32.91 μg/L) owned the lowest. Sites from upstream of the Xiangjiang River exhibited higher concentrations than that from midstream and downstream mainly due to the high concentrations of Zn, Cu, and As.

The average concentrations of all the selected elements were within the permissible limits of the drinking water guidelines by WHO (WHO 2008), USEPA (USEPA 2009), and Chinese standards (Chinese Ministry of Health 2007) except that of As (Table 1). Compared with the corresponding values of the priority toxic pollutants listed in the USEPA 2006 for aquatic life protection (USEPA 2006), a number of the elements with concentrations from different sampling sites exceeded the levels of the criteria maximum concentrations (CMC), i.e., Cd from S3, S4, and S5; Cr from S1 and S2; Cu

Table 1 Analysis of the mean, max, and min concentration values, and the standard deviation (SD) values of the trace elements in surface water from the Xiangjiang River, and the comparison with other studies and guidelines (unit in μg/L)

Locations		As	Cd	Cr	Cu	Pb	Se	Zn	Hg	Reference
Mean		12.24	1.34	6.61	20.33	2.29	4.64	84.57	0.04	Present study
Max		45.08	2.74	28.13	57.60	5.46	27. 28	500.21	0.07	
Min		1.26	0.18	0.36	2.79	0.74	0.41	10.76	0.02	
SD		12.57	0.79	8.42	17.68	1.51	8.38	126.39	0.02	
Yangze River, China		13.20	4.70	20.90	10.70	55.10	114.30	9.40		(Wu et al. 2009)
The upper Han River, China		14.16	2.30	8.11	13.37	9.20	9.65			(Li and Zhang 2010)
Pearl river, China			<1	2.8		29.1				(Cheung et al. 2003)
Subarnarekha River, India		3.11		0.73	8.26		2.50			(Giri and Singh 2014)
Tarkwa stream River, Ghana		30	1.30	2.65		1.40				(Asante et al. 2007)
Catalan River, Spain		2.90	1.20	2.40	1.30	2.20	2.40	1.90	0.80	(Carafa et al. 2011)
Tigris River, Turkey		2.35	1.37	<5	165	0.34		37		(Varol and Sen 2012)
Background concentrations, World average			0.02	1	1	0.20		10		(Klavinš et al. 2000)
Freshwater quality criteria for protection of aquatic life										(USEPA 2006)
CMC, acute		340	2	16	13	65	-	120	1	
CCC, chronic		150	0.25	11	9	3	5	12	1	
Water quality criteria for drinking water										
WHO		10	3	50	2000	10	10		1	(WHO 2008)
Chinese standards (GB5749-2006)		10	5	50	1000	10	10	1000	1	(Chinese Ministry of Health 2007)
USEPA	MCLG 0	0	5	100	1300	0	50	2000	2	(USEPA 2009)
	MCL 10	10	5	100	1300	15	50	2000	2	

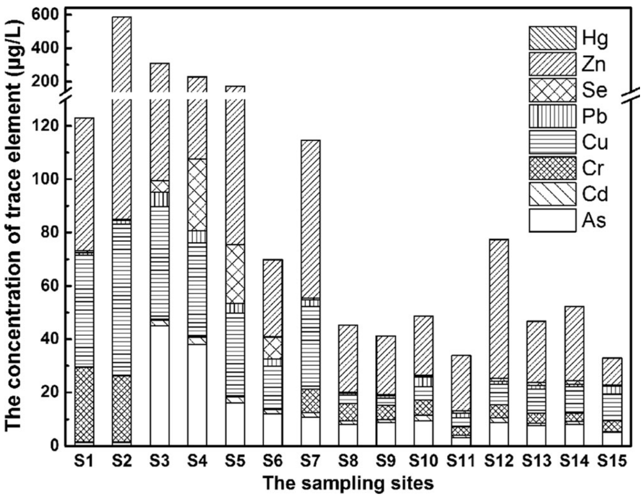

Fig. 2 Total concentrations of the trace elements in the sampling sites (μg/L)

from S1 to S7; and Zn from S2, S3, and S4. In addition, there were 93.33, 80.00, 66.67, 33.33, 20.00, and 13.33 % out of all sampling sites exceeding the criterion continuous concentration (CCC) values for Zn, Cd, Cu, Pb, Se, and Cr, respectively.

According to the average world background values, it was indicated that the mean concentrations of the trace elements in surface water from the Xiangjiang River were much higher than their corresponding world background values (Table 1). This was especially true for the cases of Cd and Cu, which were 67.10 and 20.33 times of the average world background concentrations, respectively. Comparing the trace elements concentrations data of the Xiangjiang River with the published data of other rivers at home and abroad (Table 1), it was revealed that the trace elements in surface water from the Xiangjiang River were in the moderate concentration level relatively. Generally, trace elements in surface water from the river in China exhibited higher concentrations than that from the river abroad. However, compared with the domestic rivers, the concentrations of Cu and Zn in surface water from the Xiangjiang River were higher than that from the Yangze River (the trunk stream of the Xiangjiang River and the biggest river in China), and the concentrations of Cd and Cr were higher than that from the Pearl River (the biggest river in South China), respectively.

Health risks for exposure to the trace elements

Health risk assessment was applied to detect the risk level of the trace elements in surface water from the Xiangjiang River. Calculated hazard quotients (HQs) values, hazard index (HI) values, and carcinogenic risk values of the trace elements via the oral and dermal pathways for adult and child are presented in Tables 2 and 3 and Fig. 3, respectively.

The degrees of the mean hazard quotients (HQs) decreased in the order of As > Cd > Cr > Pb > Se > Cu > Zn > Hg. The level of risk was significantly higher for child (Tables 2 and 3), indicating that children were even more vulnerable to experience the risks of the non-carcinogenic effects than the adults. For absorbing across the gastrointestinal tract and contacting with the organs of human body directly, the oral intake was the primary exposure pathway, which was consistent with the results in the other previous studies (De Miguel et al. 2007; Wu et al. 2009). According to Tables 2 and 3, HQ_{ing} (hazard quotients of ingestion) of As at 80 and 40 % out of the sampling sites exceeded unity for child and adult, respectively. It suggested that As had potential non-carcinogenic concerns for both child and adult while the rest of the elements may not cause to the residents via oral intake. Site S3 owned the highest health risks posed by As via oral intake, which were 9.81 times and 4.87 times of what were considered safe for adult and child, respectively. The elevated concentration of As was likely due to the drainage from the industrial wastewaters (Winterbourn et al. 2000; Younger et al. 2006), which would increase the risks of skin damages or the problems with circulatory systems including hypertension, neuropathy, diabetes, and cardiovascular and cerebrovascular diseases through high intake (Wu et al. 2009). The values of HQ_{derm} (hazard quotients of dermal absorption) of all the studied elements were below unity for both adult and child at all of the sites, which indicated that the concentrations of these elements may pose little or no non-carcinogenic health risks via dermal adsorption generally. Site S1 owned the largest total value of HQ_{derm}, and S11 owned the smallest. The values of HQ_{derm} for child and adult were similar. The largest value of HQ_{derm} was 0.13, which was belonged to Cr for child at S1.

The calculated HI values determined by the mixed trace elements concentrations from the sampling sites (Fig. 3) were in the descending order of S3, S4, S5, S6, S7, S10, S12, S9, S8, S14, S13, S15, S2, S1, and S11. According to the HI values, there were 93.33 and 73.33 % out of all the sampling sites in the study areas at risks of non-carcinogenic effects from the mixed trace elements for child and adult, respectively. Only the HI values at site S11 were below the limit for both child and adult. In Xiangjiang River basin, the mean value of HI for child was twice as much as that for adult. Both the mean values of HI_{ing} for child (3.21) and adult (1.60) belonged to risk level with dominant contribution to HI of As, followed by that of Cd and Cr. However, the mean values of HI_{derm} (there were 0.054 and 0.049 for child and adult, respectively) were found to be within the permissible level. Besides, the contributions to HI_{derm} of Cu, Pb, Zn, and Hg for both adult and child were negligible. Detailed comparisons were clearly presented in Fig. 3.

Among the studied carcinogenic elements, As posed the carcinogenic risks to both child and adult from the sites in upstream and midstream of the Xiangjiang River. The

Table 2 Hazard quotient of the trace element in surface water from the Xiangjiang River for child

Site	As		Cd		Cr		Cu		Pb		Se		Zn		Hg	
	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d
S1	2.72E-01	7.64E-04	2.88E-02	1.53E-03	6.12E-01	1.31E-01	6.86E-02	9.14E-04	4.67E-02	4.15E-05	6.54E-03	5.81E-04	1.09E-02	8.71E-05	8.59E-03	1.72E-04
S2	3.05E-01	8.56E-04	2.29E-02	1.22E-03	5.37E-01	1.14E-01	9.32E-02	1.24E-03	6.07E-02	5.39E-05	7.06E-03	6.27E-04	1.09E-01	8.71E-04	9.15E-03	1.83E-04
S3	9.81E+00	2.75E-02	2.78E-01	1.48E-02	1.04E-02	2.21E-03	6.86E-02	9.14E-04	2.55E-01	2.26E-04	5.75E-02	5.11E-03	4.58E-02	3.66E-04	1.31E-02	2.61E-04
S4	8.28E+00	2.32E-02	3.58E-01	1.91E-02	8.94E-03	1.90E-03	5.72E-02	7.62E-04	2.07E-01	1.84E-04	3.53E-01	3.14E-02	2.62E-02	2.09E-04	1.55E-02	3.09E-04
S5	3.49E+00	9.78E-03	2.93E-01	1.56E-02	9.99E-03	2.13E-03	5.07E-02	6.75E-04	1.75E-01	1.55E-04	2.88E-01	2.55E-02	2.11E-02	1.69E-04	1.18E-02	2.35E-04
S6	2.62E+00	7.33E-03	1.93E-01	1.03E-02	7.81E-03	1.66E-03	2.62E-02	3.48E-04	1.30E-01	1.15E-04	1.07E-01	9.52E-03	6.32E-03	5.05E-05	1.26E-02	2.53E-04
S7	2.36E+00	6.62E-03	2.16E-01	1.15E-02	1.92E-01	4.09E-02	5.07E-02	6.75E-04	1.19E-01	1.05E-04	8.20E-03	7.28E-04	1.29E-02	1.03E-04	5.89E-03	1.18E-04
S8	1.78E+00	4.99E-03	1.80E-01	9.58E-03	1.39E-01	2.97E-02	4.98E-03	6.64E-05	3.45E-02	3.07E-05	5.30E-03	4.71E-04	5.48E-03	4.38E-05	5.45E-03	1.09E-04
S9	1.91E+00	5.35E-03	1.56E-01	8.30E-03	1.11E-01	2.37E-02	4.56E-03	6.08E-05	3.83E-02	3.40E-05	6.08E-03	5.40E-04	4.82E-03	3.85E-05	5.66E-03	1.13E-04
S10	2.05E+00	5.74E-03	2.60E-01	1.39E-02	1.26E-01	2.69E-02	8.01E-03	1.07E-04	1.77E-01	1.57E-04	6.76E-03	6.00E-04	4.86E-03	3.88E-05	5.45E-03	1.09E-04
S11	6.80E-01	1.91E-03	1.20E-01	6.38E-03	6.97E-02	1.49E-02	5.50E-03	7.33E-05	7.16E-02	6.36E-05	1.22E-02	1.08E-03	4.54E-03	3.62E-05	5.45E-03	1.09E-04
S12	1.90E+00	5.32E-03	2.43E-01	1.30E-02	1.05E-01	2.23E-02	1.27E-02	1.70E-04	5.09E-02	4.52E-05	1.49E-02	1.32E-03	1.13E-02	9.06E-05	5.67E-03	1.13E-04
S13	1.66E+00	4.64E-03	1.28E-01	6.83E-03	8.06E-02	1.72E-02	1.47E-02	1.96E-04	6.21E-02	5.52E-05	1.43E-02	1.27E-03	5.01E-03	4.01E-05	5.23E-03	1.05E-04
S14	1.79E+00	5.01E-03	1.44E-01	7.66E-03	6.32E-02	1.35E-02	1.63E-02	2.18E-04	4.06E-02	3.61E-05	1.71E-02	1.52E-03	6.10E-03	4.88E-05	5.23E-03	1.05E-04
S15	1.12E+00	3.15E-03	2.69E-02	1.43E-03	8.72E-02	1.86E-02	1.63E-02	2.18E-04	1.40E-01	1.24E-04	6.86E-03	6.10E-04	2.18E-03	1.74E-05	4.36E-03	8.71E-05

HQ_i is the abbreviation of the hazard quotient of ingestion of water (unitless)

HQ_d is the abbreviation of the hazard quotient of dermal absorption of water (unitless)

Table 3 Hazard quotient of the trace element in surface water from the Xiangjiang River for adult

Site	As		Cd		Cr		Cu		Pb		Se		Zn		Hg	
	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d	HQ_i	HQ_d
S1	1.35E-01	6.99E-04	1.43E-02	1.40E-03	3.04E-01	1.19E-01	3.41E-02	8.36E-04	2.32E-02	3.79E-05	3.25E-03	5.31E-04	5.41E-03	7.97E-05	4.26E-03	1.57E-04
S2	1.51E-01	7.83E-04	1.14E-02	1.12E-03	2.67E-01	1.05E-01	4.62E-02	1.14E-03	3.01E-02	4.93E-05	3.51E-03	5.74E-04	5.41E-02	7.97E-04	4.54E-03	1.67E-04
S3	4.87E+00	2.52E-02	1.38E-01	1.35E-02	5.14E-03	2.02E-03	3.41E-02	8.36E-04	1.26E-01	2.07E-04	2.86E-02	4.67E-03	2.27E-02	3.35E-04	6.49E-03	2.39E-04
S4	4.11E+00	2.12E-02	1.78E-01	1.75E-02	4.44E-03	1.74E-03	2.84E-02	6.97E-04	1.03E-01	1.68E-04	1.75E-01	2.87E-02	1.30E-02	1.91E-04	7.68E-03	2.83E-04
S5	1.73E+00	8.94E-03	1.46E-01	1.43E-02	4.96E-03	1.95E-03	2.52E-02	6.17E-04	8.67E-02	1.42E-04	1.43E-01	2.34E-02	1.05E-02	1.55E-04	5.84E-03	2.15E-04
S6	1.30E+00	6.71E-03	9.57E-02	9.40E-03	3.88E-03	1.52E-03	1.30E-02	3.19E-04	6.43E-02	1.05E-04	5.32E-02	8.71E-03	3.14E-03	4.62E-05	6.27E-03	2.31E-04
S7	1.17E+00	6.06E-03	1.07E-01	1.05E-02	9.52E-02	3.74E-02	2.51E-02	6.17E-04	5.89E-02	9.63E-05	4.07E-03	6.66E-04	6.40E-03	9.43E-05	2.92E-03	1.08E-04
S8	8.83E-01	4.56E-03	8.93E-02	8.77E-03	6.92E-02	2.72E-02	2.47E-03	6.07E-05	1.71E-02	2.80E-05	2.63E-03	4.31E-04	2.72E-03	4.01E-05	2.70E-03	9.96E-05
S9	9.46E-01	4.89E-03	7.74E-02	7.59E-03	5.52E-02	2.17E-02	2.27E-03	5.56E-05	1.90E-02	3.11E-05	3.02E-03	4.94E-04	2.39E-03	3.52E-05	2.81E-03	1.03E-04
S10	1.02E+00	5.25E-03	1.29E-01	1.27E-02	6.27E-02	2.46E-02	3.97E-03	9.76E-05	8.76E-02	1.43E-04	3.35E-03	5.49E-04	2.41E-03	3.55E-05	2.70E-03	9.96E-05
S11	3.38E-01	1.74E-03	5.94E-02	5.83E-03	3.46E-02	1.36E-02	2.73E-03	6.70E-05	3.55E-02	5.82E-05	6.06E-03	9.91E-04	2.25E-03	3.32E-05	2.70E-03	9.96E-05
S12	9.41E-01	4.86E-03	1.21E-01	1.19E-02	5.19E-02	2.04E-02	6.33E-03	1.55E-04	2.53E-02	4.13E-05	7.40E-03	1.21E-03	5.63E-03	8.28E-05	2.81E-03	1.04E-04
S13	8.22E-01	4.25E-03	6.36E-02	6.25E-03	4.00E-02	1.57E-02	7.30E-03	1.79E-04	3.08E-02	5.05E-05	7.08E-03	1.16E-03	2.49E-03	3.66E-05	2.60E-03	9.56E-05
S14	8.87E-01	4.58E-03	7.14E-02	7.01E-03	3.14E-02	1.23E-02	8.11E-03	1.99E-04	2.02E-02	3.30E-05	8.50E-03	1.39E-03	3.03E-03	4.46E-05	2.60E-03	9.56E-05
S15	5.58E-01	2.88E-03	1.33E-02	1.31E-03	4.33E-02	1.70E-02	8.11E-03	1.99E-04	6.95E-02	1.14E-04	3.41E-03	5.58E-04	1.08E-03	1.59E-05	2.16E-03	7.97E-05

HQ_i is the abbreviation of the hazard quotient of ingestion of water (unitless)

HQ_d is the abbreviation of the hazard quotient of dermal absorption of water (unitless)

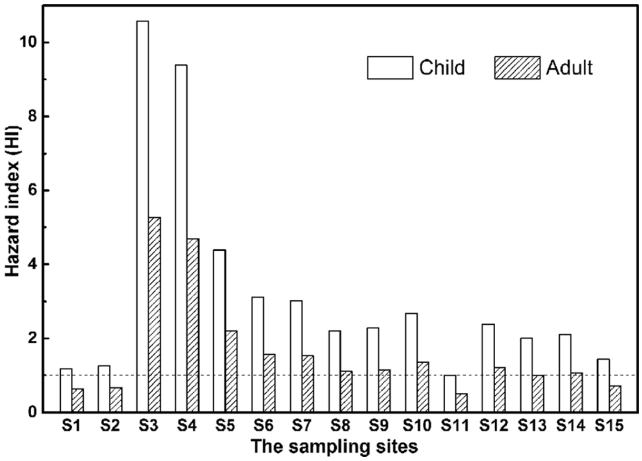

Fig. 3 Hazard index of the mixed trace elements in surface water from the Xiangjiang River (*dotted line* is the acceptable limit of HI)

carcinogenic risks for exposure to As ranged from 1.23×10^{-4} to 4.42×10^{-3} for child and ranged from 6.12×10^{-5} to 2.20×10^{-3} for adult. It exceeded the target risk of 1×10^{-4} under most regulatory programs mainly through oral intake at sites S3 to S7 for child and at sites S3 and S4 for adult, respectively (Chen and Liao 2006; Liao and Chiang 2006). It was indicated that ingesting surface water from the Xiangjiang River over a long life time could increase the probability of cancers which closely related to high As intake, such as the cancers of liver, lung, bladder, kidney, and skin (Avani and Rao 2007; Bhattacharya et al. 2007). According to the results of hazard quotients (HQs) and carcinogenic risk assessment, As was the most important pollutant in the Xiangjiang River, which was similar to the previous researches compared with in Table 1 (Giri and Singh 2014; Li and Zhang 2010; Wu et al. 2009). Therefore, it is required to design and apply a systematic method for monitoring the exposure of As which might be more likely to cause severe health risks to the local residents, particularly the sensitive children, than the other studied trace elements.

Multivariate statistical analysis of the trace elements

Correlation matrix

The correlations among trace elements can provide some information on the sources and the emission pathways of them. A correlation matrix was calculated by the Pearson's correlation coefficients for the trace elements in surface water from the Xiangjiang River, and the results were showed in Table 4. A number of significant positive correlations existed among the selected elements (The element pairs As-Cd, As-Pb, As-Hg, Cd-Cr, Cd-Se, Cu-Zn, Pb-Hg, and Se-Hg had a significantly positive correlation at <0.01 significance level, and the element pairs As-Se, Pb-Cd, Cu-Cr, Hg-Cu, and Pb-Se had a significantly positive correlation at <0.05 significance level. Based on the published studies (Lu et al. 2010; Saeedi et al. 2012), if the correlation coefficient between the element factors is positive, these factors may have common source, mutual dependence, and identical behavior during the transport.

Principal component analysis

Principal component analysis (PCA) was applied to the data sets of the selected elements concentrations separately from the 15 sampling sites to identify their similar behavior and common origin by employing varimax rotation with Kaiser Normalization. The value of KMO was 0.69 and the significance of Bartlett's sphericity test was less than 0.01, which indicated that the PCs analysis was effective for the studies (Varol 2011).

PCA of the entire data set (Table 5) revealed two PCs with eigenvalues >1 that explained about 81.63 % of the total variance in the trace elements concentrations data set. The coefficients performed on the PCs having a correlation greater than 0.70 were considered to be significant variables influencing the water quality. The first component (PC1) that explained 50.41 % of the total variance was dominated by As, Cd, Pb, Se, and Hg with strong positive loadings. The second factor (PC2) demonstrated high loadings of Zn, Cu, and Cr and elucidated 31.23 % of the total variance (Table 5). The results of PCA were well matched with the results of Pearson's correlation analysis.

Cluster analysis

Cluster analysis (CA) was applied to the trace elements concentrations data set to identify spatial variability. Since we used hierarchical agglomerative cluster analysis, the cluster classifications varied with significance level and were also decided by water environment quality which was mainly affected by land use and industrial structure. The sites in the clusters had similar characteristics and anthropogenic/natural background source types (Varol and Sen 2012). CA rendered a dendrogram (Fig. 4) which all 15 sampling sites from the river were grouped into three statistically significant clusters at $(D_{link}/D_{max})\times25<5$. Cluster 1 consisted of three sites (S3, S4, and S5) was corresponded to sites with a high concentration level of As and Cd, which were probably taken as the high contaminated sites. Cluster 2 consisted of two sites (S1 and S2) was corresponded to sites with prominent concentrations of Cu and Zn compared with the other elements, which might be explained as the low pollution regions. Cluster 3 consisted of ten sites (including the rest of the sites), which were situated in midstream and downstream of the river. And the elements from these sites were of relatively moderate concentrations with small spatial variability compared to that from the other sites and were in the relatively moderate pollution degree.

Table 4 Pearson's correlation matrix for the trace elements in surface water from the Xiangjiang River

	As	Cd	Cr	Cu	Pb	Se	Zn	Hg
As	1.000	0.734**	−0.490	0.328	0.799**	0.595*	0.152	0.729**
Cd		1.000	−0.658**	−0.048	0.621*	0.649**	−0.164	0.500
Cr			1.000	0.531*	−0.437	−0.381	0.469	−0.128
Cu				1.000	0.341	0.310	0.782**	0.634*
Pb					1.000	0.573*	0.133	0.652**
Se						1.000	0.078	0.784**
Zn							1.000	0.391
Hg								1.000

*Correlation significant at the 0.01 level (two tailed)

**Correlation significant at the 0.05 level (two tailed)

Similarly, CA was performed to identify the relationships among the analyzed trace elements and their possible sources. CA rendered a dendrogram in Fig. 5, where all eight trace elements were grouped into two statistically significant clusters at (Dlink/ Dmax)×25<10. Cluster 1 contained Zn which was found in the high concentration level. Cluster 2 included the elements of Cd, Hg, Pb, Se, Cr As, and Cu, which were identified in the moderate concentration levels relatively and also reflected by the significantly correlations (Table 4).

Source identification of the trace elements

Two main sources of the trace elements in surface water from the Xiangjiang River could be identified by spatial distribution, correlation coefficient analysis, PCA, and CA, i.e., (1) As, Cd, Pb, Se and Hg, which were mainly identified as contaminants derived from the chemical industrial effluents and the coal burning; (2) Zn, Cu, and Cr, which were mainly originated from the natural erosion, the mineral exploitation activities and the non-point agricultural sources.

Table 5 Total variance explained and component matrix for the trace elements in surface water from the Xiangjiang River

Element	Component	
	PC1	PC2
As	0.908	0.080
Cd	0.849	−0.302
Cr	−0.592	0.718
Cu	0.271	0.936
Pb	0.853	0.099
Se	0.825	0.102
Zn	0.068	0.879
Hg	0.807	0.465
Eigenvalues	4.033	2.498
% of total variance explained	50.409	31.225
% of cumulative variance	50.409	81.634

PCA with Varimax rotation, KMO=0.692 and the significance of Bartlett's sphericity test is <0.01

One group of elements, including As, Cd, Pb, Se, and Hg, which indicated strong associations in Pearson's correlation analysis, PCA and CA (Tables 4 and 5 and Fig. 5), had a similar spatial distribution with the high polluted sites mainly located in the upstream and midstream of the Xiangjiang River. The industrial enterprises produced vast millions tons of wastewaters yearly, in which the toxic metals and elements were more than 5000 tons, mainly composed of Cd, Pb, As, Hg, and other metals. But there were only less than 70 % of the wastewaters went through the integrated wastewater treatment, which had led to environmental pollutions to the corresponding ecosystem, the geomorphologic landscape, the soil, and the water environment, especially the water environment (Li et al. 2013). According to the published researches (Chai et al. 2010; Li et al. 2014; Peng et al. 2011; Zhu et al. 2012), the Xiangjiang River had been polluted by heavy metals and trace elements which mainly came from chemical industrial manufacturing and heavy industry. The elements, such as As, Cd, and Pb, were widely used in electroplating industry, chemical industry, electronics industry, and other fields. They were the industrial raw materials applied to glass, ceramics, electronics, leather, textile, fertilizer, etc. The multitudinous chemical enterprises (such as the

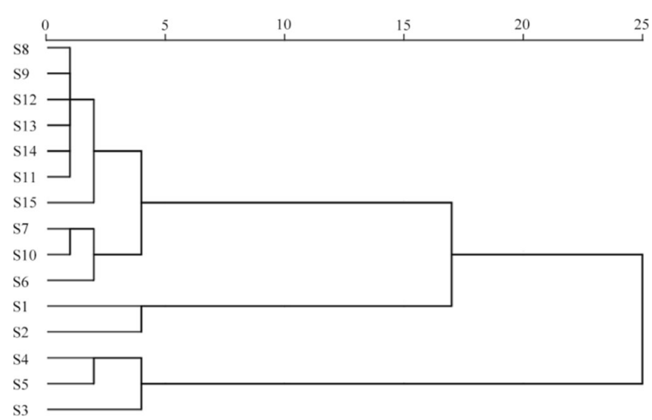

Fig. 4 Dendrogram of the sampling sites from the Xiangjiang River

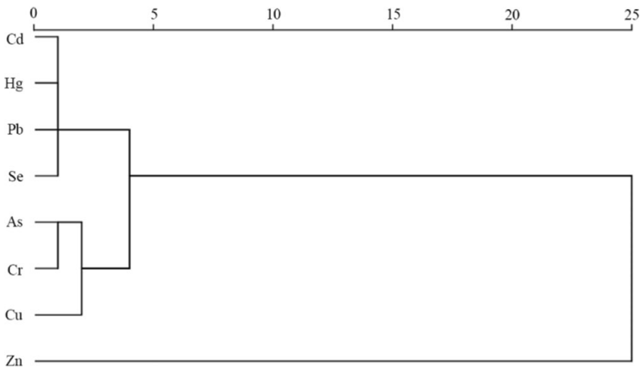

Fig. 5 Dendrogram of the trace element concentrations in surface water from the Xiangjiang River

Zhuzhou smelting group, the ShuiKouShan nonferrous metals group, the Hunan Hayley chemical group, the Hualing steel enterprise, the Huaxin cement plant, the coal power plants, and lots of small chemical enterprises) which were attracted to locate in the Xiangjiang River basin, especially in the Hengyang City and the Zhuzhou City, could be considered as the biggest anthropogenic sources of those trace elements emissions in the surface water. Sites S3, S4, and S5 were in the highest concentrations of the polluted elements in this study.

The second group of elements was consisted of Zn, Cu, and Cr, which had significantly positive correlations in Pearson's correlation analysis and PCA (Tables 4 and 5). They mainly derived from the mixed sources of the natural erosion, the mineral exploitation activities, and the non-point agricultural sources. Being one of the mineralized areas where the resources of Zn and Cu were found abundant in the Earth's crust, the regions in the upstream of the Xiangjiang River basin, especially in the Yongzhou City, were under tremendous pressure of resources exploitation. It was inferred that the source from the natural factor was mainly because of the high concentration background levels of Zn and Cu in the Xiangjiang River. However, their concentrations were higher at sites near the mining industries in upstream. Therefore, Zn and Cu could come from both natural and anthropogenic sources. The mining industries (including corresponding industries of mining, beneficiation, smelting, and machining) of the studied area which made the biggest contribution for the local gross industrial output values were responsible for governing the high concentration levels of Cu and Zn in the surface water. Further, the spatial contents of Cr and Cu, which indicated strong associations in correlation coefficient analysis, PCA and CA, were probably in relationship with the spatial distribution characteristics of agriculture land. Sewage irrigation and increasingly applying kinds of pesticides, which contained lots of the heavy metals, represented non-point source pollution from orchards and agriculture areas of the basin. They were deemed to enhance the contents of Cr and Cu in the wastewaters.

Conclusions

When compared to the water quality criteria recommended by China, WHO and USEPA, much greater attention should be paid to As for its mean concentration exceeded the critical values; however, the other trace elements were in the acceptable ranges. According to the health risk assessment, it was indicated that As was identified as the priority pollutant of concerns among the studied trace elements, causing both non-carcinogenic and carcinogenic effects. Children were more sensitive to the risks compared to the adults and the oral intake was the primary exposure pathway. As a whole, the highest risks for exposure to the trace elements in the surface water were occurred in the upstream of the Xiangjiang River. The mixed trace elements may compromise the water quality of the Xiangjiang River and had the potential to posed integrated chronic risks to the human health, especially in low-income communities that make direct use of the untreated river water.

Multivariate statistical analyses revealed the correlations of the trace elements which cannot be viewed in isolation. It was reasonable to conclude that anthropogenic activities were major contributing factors as sources of the trace elements in the Xiangjiang River. The spatial characteristics of the trace elements were found in the close relationships with that of the mineral exploitation, the industrial activities, and the non-point agricultural sources along the Xiangjiang River.

Therefore, to guarantee the public health and safety of the sensitive receptors, it is necessary to make regular monitoring and assessment of exposure to the trace elements in aquatic systems. And emergently, developing contamination control management (especially the contamination control management of the wastewaters with As) of the corresponding cities, must be add into the calendar of the restoration of the Xiangjiang River.

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