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Risk analysis of heavy metal concentration in surface waters across the rural-urban interface of the Wen-Rui Tang River, China☆

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ABSTRACT

Heavy metal pollution is a major concern in China because of its serious effects on human health. To assess potential human health and ecological risks of heavy metal pollution, concentration data for seven heavy metals (As, Pb, Cd, Cr, Hg, Cu, Zn) from 14 sites spanning the rural-urban interface of the Wen-Rui Tang River watershed in southeast China were collected from 2000 to 2010. The heavy metal pollution index (HPI), hazard index (HI) and carcinogenic risk (CR) metrics were used to assess potential heavy metal risks. Further, we evaluated the uncertainty associated with the risk assessment indices using Monte Carlo analysis. Results indicated that all HPI values were lower than the critical level of 100 suggesting that heavy metal levels posed acceptable ecological risks; however, one site having an industrial point-source input reached levels of 80–97 on several occasions. Heavy metal concentrations fluctuated over time, and the decrease after 2007 is due to increased wastewater collection. The HI suggested low non-carcinogenic risk throughout the study period (HI < 1); however, nine sites showed CR values above the acceptable level of 10^{-4} for potential cancer risk from arsenic in the early 2000s. Uncertainty analysis revealed an exposure risk for As at all sites because some CR values exceeded the 10^{-4} level of concern; levels of Cd near an old industrial area also exceeded the Cd exposure standard (2.6% of CR values > 10^{-4}). While most metrics for human health risk did not exceed critical values for heavy metals, there is still a potential human health risk from chronic exposure to low heavy metal concentrations due to long-term exposure and potential metal interactions. Results of this study inform water pollution remediation and management efforts designed to protect public health in polluted urban area waterways common in rapidly developing regions.

1. Introduction

Heavy metal pollution in aquatic environments has received considerable global attention due to its potential to cause irreversible damage to human health (Chowdhury et al., 2016; Ali et al., 2016). Heavy metals are considered systemic toxicants that may lead to multiple organ damage along with teratogenic and carcinogenic effects (Tchounwou et al., 2012). Long-term exposure to heavy metals has also been implicated in causing permanent intellectual and developmental disabilities, behavioral problems, hearing loss, learning and attention problems, and disruption of visual and motor function (Sarkar, 2009). Even at low-levels of exposure (i.e., chronic exposure) arsenic can cause skin and lung cancer while chronic cadmium exposure is linked to breast and ovarian cancer (Hong et al., 2014; Adams et al., 2014). Further, interactions associated with exposure to multiple heavy metals may induce more severe human health consequences than might be expected from low individual metal concentrations alone.

Exposure to heavy metals from water bodies also occurs through bioaccumulation of metals in human food sources (Baby et al., 2010; Krishnamurti et al., 2015; Fazio et al., 2014). Thus, even if humans do not consume heavy-metal tainted water directly, they

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are often exposed to high levels of heavy metals from plant and aquatic food sources grown in the polluted waters (Jiang et al., 2016; Antoniadis et al., 2017a; Antoniadis et al., 2017b). This is especially important in rapidly developing areas of Asia where locally grown food represents a large fraction of the food supply in urban centers.

Heavy metals in rivers may originate from both natural and anthropogenic processes, such as mineral weathering, industrial and domestic municipal wastes, wastes from domesticated animals receiving metals in food supplements, and atmospheric deposition (Reza and Singh, 2010). In general, the largest source of heavy metals in aquatic ecosystems resides in the sediments, with much lower concentrations dissolved in the water column (Gaur et al., 2005). Thus, most previous studies have focused on heavy metal dynamics in sediments rather than in the water column (Davutluoglu et al., 2011; Liu et al., 2015; Kuang et al., 2016; Tang et al., 2016; Pan et al., 2017). However, heavy metals released from the sediment are a primary control on metal concentrations in the water column (Huang et al., 2012) and metal concentrations and speciation in the water column dictate metal availability to organisms (e.g., fish & humans). Therefore, greater attention needs to be focused on heavy metals in surface waters due to its potential to affect human health exposure to heavy metals through food, water and body contact pathways.

Previous studies concerning the potential health risk caused by heavy metals in surface waters used the human health risk assessment method recommended by the United States Environmental Protection Agency (US-EPA) to calculate a quantitative health risk value. This method used chronic daily intake and corresponding absorption coefficients to estimate potential human health risks (Wu et al., 2009; Li et al., 2014; Yang et al., 2015). Heavy metal pollution index was used to analyze the potential ecological risk to the environment (Mohan et al., 2008). Additionally, many complementary methods have been used to strengthen the analysis efficiency. Multivariate statistical analyses to determine heavy metal sources (Race et al., 2015) and geographic information system (GIS) techniques have also been used to assess the spatial distribution of pollutants and determine input sources (Tiwari et al., 2015; Tiwari et al., 2016). Previous studies of heavy metal risk assessment rarely consider spatial-temporal variations in heavy metal pollution. Rather, they usually rely on deterministic evaluations that often result in the loss of some important information. Therefore, a long-term, comprehensive evaluation of the uncertainties associated with human health risk assessments of heavy metals is necessary.

The Wen-Rui Tang River watershed is located in Wenzhou, Zhejiang Province on the east coast of China. The watershed has suffered severe environmental deterioration due to rapid economic development coupled with lagging infrastructure to protect the environment. Research to date in the Wen-Rui Tang River watershed has primarily focused on the effects of nitrogen and phosphorus (Mei et al., 2014; Chen et al., 2016), polycyclic aromatic hydrocarbons and organic carbon (Li et al., 2016) in the hypoxic/anoxic waterways. In addition, Gu et al. (2012) and Song et al. (2012) examined the ecological risk of sediments in the Wen-Rui Tang River network. However, these previous studies did not assess the risk of heavy metal pollution on human health. Therefore, this study was designed to provide a comprehensive assessment of potential environmental and human-health risks from heavy metals in the Wen-Rui Tang River watershed. Specific objectives of this study were: (1) to assess spatial distribution and temporal trends in heavy metal concentrations in surface waters of the Wen-Rui Tang River watershed; and (2) to evaluate potential human health risks and uncertainties associated with various assessment metrics. The results of this study will inform water pollution agencies with quantitative data to guide water quality remediation and health agencies with scientific data to better protect humans from heavy metal exposure.

2. Materials and methods

2.1. Study area

The Wen-Rui Tang River watershed, with a drainage area of approximately 370 km^2, lies between 27°52' - 28°4′N latitude and 120°28' - 120°46′ E longitude at an average elevation of 100 m (Fig. 1). The basin has an average annual temperature of 18 °C and average annual rainfall of 1695 mm with approximately 70% falling between April and September. Annual river runoff is 913 million m^3 and reservoir storage capacity is 65 million m^3. The basin has a population of ~9.2 million with large variations in population density − from rural to densely populated urban centers (WSB, 2010).

The Wen-Rui Tang River is a critical irrigation and drainage channel for 32,100 ha farmland and aquaculture in the Wen-Rui plain and also the major water source for residents and industrial/mining enterprises along the river. With rapid development of the Wenzhou economy, the hardware, electroplating, leather and shoe industries became highly concentrated within the watershed. Heavy metal pollution became very severe due to direct disposal of untreated domestic and industrial wastewaters into the river. No more than ~60% of the average sewage load was collected for centralized processing at wastewater treatment facilities in the 2000s (Fig. 2a). Local governments initiated a series of pollution control measures since 2000, such as improved sewage collection, establishment of industrial parks with sewage treatment facilities, removal of river sediments, and riparian green landscape construction, to address heavy metal and other water quality concerns (Mei et al., 2014).

2.2. Data collection and data quality assessment

Eleven years of water quality data from 2000 to 2010 were obtained for 14 river monitoring sites from the Wenzhou Environmental Protection Bureau (WEPB). Data were collected every two-month to determine As, Pb, Cd, Cr and Hg concentrations and several conventional water quality indicators (pH, dissolved oxygen, chemical oxygen demand, ammonia-nitrogen, total nitrogen, total phosphorus, etc.). Data for Zn and Cu were added to the analyses in 2009 and 2010. Four monitoring sites were located in rural areas (A5, B1, B2 and B3), while the remaining 9 sites were in urban areas (Figure 1). Monitoring sites were selected to represent various land-use patterns and anthropogenic activities (Fig. 2b). Sampling, preservation and analysis protocols strictly followed standard methods (China MEP, 2009). All samples were collected and preserved in pre-acid washed plastic bottles. Samples were filtered through a 0.45 μm cellulose nitrate membrane filter, acidized to pH = 1−2 with diluted HNO_3, and stored at −4 °C prior to analysis. All plastic and glass containers were acid washed by soaking in diluted HNO_3 for at least 24 h. Copper, Zn, Pb, Cd and Cr was measured by atomic absorption spectrometry; As and Hg was measured by atomic fluorescence spectrometry. All samples were analyzed in duplicate and relative standard deviations were within ±5%. Chinese National Standard Materials (BW-0610−0614 for Pb, As, Cu, Zn, Cd; BW-0617 for Cr; GBW-08617 for Hg) were used to determine the accuracy of the analytical procedures; recovery rates were within ±15% for all metals. To facilitate statistical analyses, heavy metals concentrations lower than detection limits were set to the detection limit value, rather than zero, for analyses (Yang et al., 2015) (Table S1). Statistical calculations for detection rates,

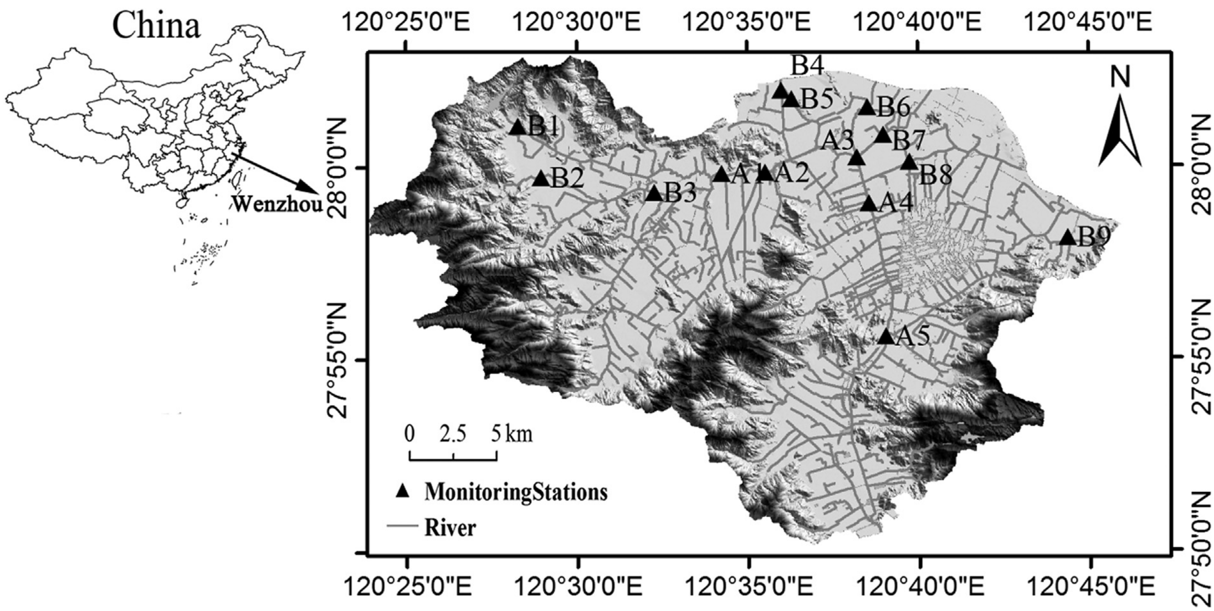

Fig. 1. Monitoring sites in the Wen-Rui Tang River basin.

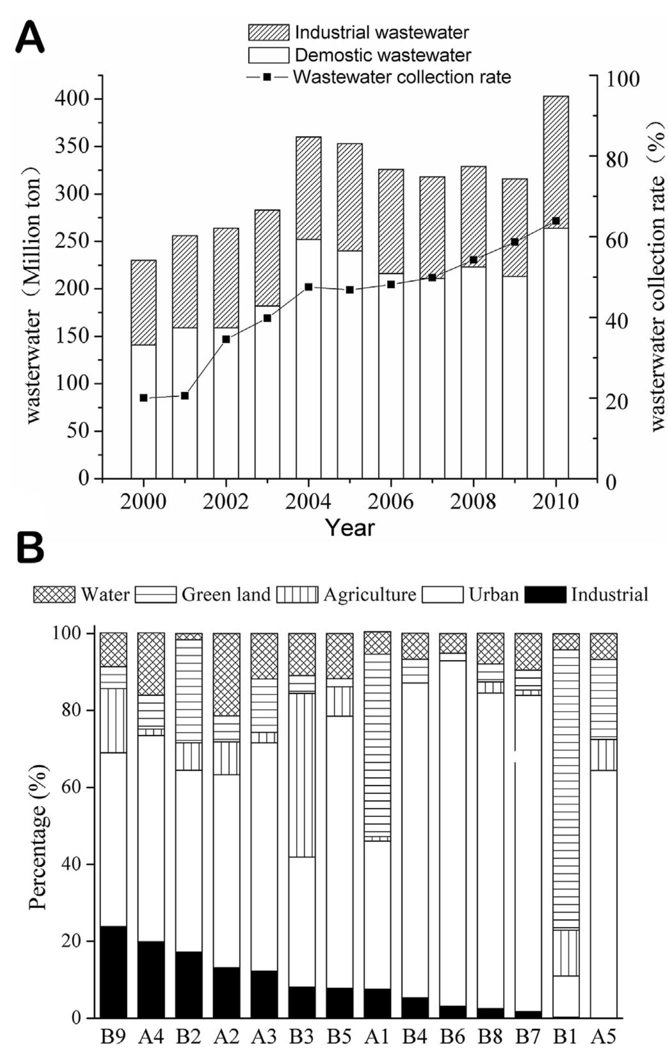

Fig. 2. (a) Wastewater discharge and collection rate in Wenzhou from 2000 to 2010; and, (b) land use pattern for 14 monitoring sites.

means, standard deviations, and standard exceedance rates were determined using SPSS 20.0.

2.3. Heavy metal pollution index

The heavy metal pollution index (HPI) is a rating model that provides the composite influence of individual heavy metals on overall water quality. The HPI model (Mohan et al., 2008) is given by Eq. (1)

$$HPI = \frac{\sum_{i=1}^{n}(Q_i W_i)}{\sum_{i=1}^{n} W_i} \tag{1}$$

Where, is the sub-index of the ith heavy metal parameter, is the unit weight of the ith parameter reflecting its relative importance, and n is the number of parameters considered. The sub-index (Q_i) is calculated by Eq. (2)

$$Q_{i=} = \frac{c_i}{s_i} \times 100 \tag{2}$$

Where c_i is the concentration value of the ith heavy metal parameter (μg L^{-1}), and s_i is the highest standard permissible value of the ith parameter. We selected the World Health Organization (WHO) Guidelines for drinking-water quality (WHO, 2017) as the source of the highest standard permissible level.

The unit weight (W_i) of the parameter is calculated by Eq. (3)

$$W_i = \frac{k}{s_i} \tag{3}$$

Where k is a proportionality constant. In order to facilitate calculation, we set k to 1 as Wanda et al. (2012). Generally, the critical HPI value for drinking water is 100 (Prasad and Bose, 2001). However, a modified scale using three classes is often used to better characterize moderate levels of heavy metal pollution (Edet and Offiong, 2002): low (HPI values < 15), medium (HPI values within 15–30) and high (HPI values > 30).

The temporal trend of total heavy metal pollution was assessed using annual average HPI values for both urban and rural sites. In addition, GIS techniques were used to spatially display the results of HPI assessments for heavy metal ecological risk within the Wen-Rui Tang River watershed. We employed an inverse distance weighted (IDW) method to interpolate values from monitoring sites to adjacent sub-basins in ArcGIS 10.2 (ESRI Inc, USA). Values for the southwest region of the study area lacked statistical credibility due to the limited monitoring data available for this area. Thus, the interpolation results for the southwest region are not shown.

2.4. Human health risk assessment model

Human exposure to heavy metals occurs through several pathways including direct ingestion, dermal absorption through skin, and inhalation through mouth and nose. Ingestion and dermal absorption are the most common pathways for drinking water (Wu et al., 2009; Li and Zhang, 2010). The US-EPA points out that the human body absorbed pollutant dose is calculated from chronic daily intake (CDI), which means the pollutant dose per kilogram of body weight per day that is absorbed through direct ingestion, dermal absorption or inhalation (US EPA, 2004). We used the direct ingestion and skin absorption as the main exposure pathways. The CDI of water ingestion and dermal absorption was defined as Eq. (4) and (5).

$$CDI_{in} = \frac{c_i \times IR \times ABS_g \times EF \times ED}{BW \times AT} \tag{4}$$

$$CDI_d = \frac{c_i \times SA \times K_p \times ABS_d \times ET \times EF \times ED \times CF}{BW \times AT} \tag{5}$$

Where CDI_{in} and CDI_d are exposure doses from ingestion of water and dermal absorption (μg kg^{-1}day^{-1}), respectively, and c_i is the average concentration of the *i*th heavy metal in water (μg L^{-1}). Additional explanations, values and units for other parameters are shown in Table 1. Our risk estimates for water ingestion were conservative as we replaced non-detectable metal concentrations with the analytical detection limits (Table S1) rather than using a zero value. The parameter reference values originated from the Ministry of Environmental Protection of China (China MEP) handbook (China MEP, 2013), US-EPA manual (US EPA, 2004) and WHO guidelines (WHO, 2017).

Human health risk was divided into non-carcinogenic and carcinogenic risks by the International Agency for Research on Cancer (IARC) through Hazard Quotients (HQ) and carcinogenic risk (CR), respectively. The HQ is estimated by comparing exposure or average intake of contaminants from each exposure route (ingestion & dermal in this paper) with the corresponding reference dose (RfD) using Eq. (6).

$$HQ = \frac{CDI}{RfD} \tag{6}$$

Where *RfD* (μg kg^{-1}day^{-1}) of ingestion (RfD_{in}) values for individual heavy metals originated from the US-EPA as shown in Table 1, while *RfD* of dermal absorption (RfD_d) equals RfD_{in}/ABS_d. Generally, if the exposure dose is lower than the threshold, it would not create a health risk. A $HQ > 1$ suggests that the pollution level might induce risks to human health and a $HQ < 1$ suggests no significant health risk. In this study, we used the hazard index (HI) to express the total potential health risk, which was the sum of HQs from all possible pathways. We choose a value of 1 as the threshold of concern in accordance with European Center for Ecotoxicology of Chemicals (ECEC, 2001).

Carcinogenic risks were evaluated by Eq. (7)

$$\begin{cases} CR = CDI \times SF, & CDI \times SF < 0.01 \\ CR = 1 - EXP(CDI \times SF), & CDI \times SF \geq 0.01 \end{cases} \tag{7}$$

The reference value for the cancer slope factor (SF, μg^{-1}kg day) originated from China MEP (Table 1). Following US-EPA guidance, a CR value lower than 10^{-6} represents negligible levels, values $10^{-6} < CR < 10^{-4}$ are acceptable levels, while $CR > 10^{-4}$ signifies a high cancer risk to humans. Both HI and CR were calculated using parameters from Table 1 and reflect the potential health risk probability from a lifetime exposure.

According to the IARC report (2013), the heavy metals which were carcinogenic to humans - arsenic and probably carcinogenic to humans - cadmium were considered for both carcinogenic and non-carcinogenic risk assessment. Conversely, metals which were possibly carcinogenic to humans - Pb and Hg were only included in the non-carcinogenic risk assessment (Table S3). Copper and zinc were not classified in the IARC report, but previous study showed they were necessary to humans (Chan et al., 1998), so we included them only in the non-carcinogenic risk assessment.

The IDW method was also used to interpolate CR values for the monitoring sites into a whole basin visualization of the spatial

Table 1
Parameter details for health risk assessment in the Wen-Rui Tang River basin.

Parameter	Mean Value		Units
	Rural	Urban	
Ingestion rate (IR)	1.96[a]	1.92[a]	L day^{-1}
Exposure frequency (EF)	365[a]	365[a]	days year^{-1}
Exposure duration (ED)	77.73[a]	77.73[a]	year
Body weight (BW)	59.8[a]	62.5[a]	kg
Average time (AT)	28371.5[a]	28371.5[a]	days
Skin-surface area (SA)	16000[a]	16000[a]	cm^2
Permeability coefficient (K_p)	0.002 for Cr(VI)[b] and 0.001 for other metals[b]		cm h^{-1}
Exposure time (ET)	0.236[a]	0.273 [a]	h day^{-1}
Conversion factor (CF)	10^{-3}[b]		L cm^{-3}
Gastrointestinal absorption factor (ABS_g)	1 for As[b],0.3 for Pb[c], 0.05 for Cd[b], 0.07 for Hg[b], 0.3 for Cu[b] and 0.2 for Zn[b]		
Dermal absorption factor (ABS_d)	0.03 for As[b] and 0.001 for others[b]		
Reference dose (RfD)	Ingestion: 0.3 for As[b], 1.4 for Pb[b], 0.5 for Cd[b], 0.3 for Hg[b], 40 for Cu[b] and 300 for Zn[b]		μμg kg^{-1}day^{-1}
Cancer slope factor(SF)	1.5*10^3 for As[b] and 6.1*10^3 for Cd[b]		μg^{-1} kg day

[a] Exposure factors handbook of Chinese population (China MEP, 2013)
[b] Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (US EPA, 2004)
[c] Guidelines for drinking-water quality (WHO, 2017)

distribution for carcinogenic risks. We averaged the 11 year data record into three temporal periods (Early: 2000–2003, Mid: 2004–2007, Late: 2008–2010) to examine temporal trends in heavy metal concentrations and potential effects on human health.

2.5. Monte Carlo simulation

Health risk assessment has several characteristics such as multivariate, randomness, and time-variation that directly or indirectly lead to fuzzy and uncertainty in forecast/prediction models. A Monte Carlo analysis based on mathematical statistics and probability theory was used to assess model uncertainty by random sampling of a probability distribution for each variable. The main objectives of the Monte Carlo simulation in this study were to estimate the distribution of the heavy metal concentration, ingestion rate, exposure duration, body weight and skin-surface area in order to determine a probability distribution (i.e., uncertainty) for the assessment metrics. Combining the US-EPA health risk assessment method with Monte Carlo analysis provides a probability distribution of HI and CR values to evaluate the uncertainty associated with the human health risks for heavy metal exposure (US EPA, 1997). Additionally, the sensitivity analysis was used to determine the most important factors for health risk. The sensitivity is dependent on the correlation coefficient between each parameter (e.g., C_i, IR, BW and so on) and the risk value. A higher correlation coefficient indicates a higher contribution to final health risk and the sensitivity of each factor was expressed as percentage.

The Monte Carlo analysis and sensitivity analysis was facilitated using Crystal Ball 11.1 (Oracle Inc, USA) and each parameter was fit to the closest input data distribution type as evaluated by the Anderson-Darling test, K-S test, and Chi-Square test (Gonzalez et al., 2005). The distribution of heavy metal concentrations was obtained from the available monitoring data from 2000 to 2010 (Table S2). Distribution of other parameters, including ingestion rate, exposure duration, body weight and skin-surface area, was set as normal distribution.

3. Results and discussion

3.1. Heavy metal concentration

Summary statistics for heavy metal concentrations in Wen-Rui Tang River waterways are shown in Table 2. Mean concentrations for the seven heavy metals followed the order: Zn > Cu > Cr > Pb > Cd > As > Hg. The relative abundance of heavy metals in the water column was consistent with results obtain from sediments collected within the study area (Li et al., 2017). An estimation of background concentrations for the heavy metals from Shanxi Reservoir – a drinking water source in the mountains 50 km west of Wenzhou – showed no detectable heavy metal concentrations (Huang et al., 2017). This indicates that heavy metals in the Wen-Rui Tang River watershed are derived primarily from anthropogenic activities rather than natural sources (Bednarova et al., 2013). The higher concentrations of Zn ($72.1 \pm 5.98\ \mu g\ L^{-1}$), Cu ($20.9 \pm 2.41\ \mu g\ L^{-1}$), Cr ($5.32 \pm 0.73\ \mu g\ L^{-1}$) and Pb ($4.23 \pm 0.15\ \mu g\ L^{-1}$) are likely sourced from wastewater and surface runoff receiving metals from electroplating and galvanizing facilities (Zn, Cu, Cr), leather tanning facilities (Cr), vehicle-related emissions (Zn, Pb, Cu), livestock and poultry farms (Cu, Zn), phosphate fertilizers (Cd, Hg, Pb, Zn), and atmospheric deposition (Cd, Zn) (Shomar, 2009; Thévenot et al., 2007; Meybeck et al., 2007; Sutherland, 2000; Kabas et al., 2014). Concentrations of Hg were consistently low $0.03 \pm 0.002\ \mu g\ L^{-1}$ suggesting low atmospheric deposition of Hg and fewer industrial enterprises discharging Hg to the environment.

In comparison to drinking water quality standards specified by the World Health Organization (WHO, 2017) and Ministry of Health of China (China MOH, 2006), concentrations of heavy metals in the Wen-Rui Tang River did not exceed the WHO drinking water standard, with a few exceptions (<5%) for Cd, Pb, Cr and As (Table 2). Although Cr concentrations (up to $389\ \mu g\ L^{-1}$) occasionally exceeded the WHO drinking water standard, the overall Cr concentration was at a low level (~$5\ \mu g\ L^{-1}$). The extremely high Cr values were found at sites B2 and B6 between 2002 and 2004. Because of the low overall Cr detection rate, it was excluded from further analyses.

3.2. Spatio-temporal distribution of heavy metal pollution index (HPI)

The HPI is used to characterize the potential environmental risk of heavy metals in waterbodies. The temporal (Fig. 3a) and spatial (Fig. 3b) trends for the HPI in the Wen-Rui Tang River basin were calculated based on the long-term data available for As, Cd, Pb, and Hg. The HPI values fluctuated throughout the study period (2000–2010). For the urban sites, it decreased from 2000 to 2002, increased from 2003 to 2007, and then decreased until 2010. The HPI trend in rural sites was similar to that in the urban area, with the exception of a slight decrease in the urban HPI in 2006. The average and maximum HPI values for the urban area tended to be higher than for the rural area prior to 2005 before converging to similar levels for the remainder of the study period. All HPI values were less than the critical value of 100; however, some urban HPI values exceeded values of 80 in the 2000–2005 period. After 2005, the maximum HPI values were <40 indicating a transition in heavy metal concentrations occurring around 2005. The increase of the HPI from 2002 to 2005 could be due to lagging sewage pipeline

Table 2
The Summary statistics of the heavy metal concentrations.

	Detection rate (%)	Mean ± Std. dev. ($\mu g\ L^{-1}$)	Range ($\mu g\ L^{-1}$)	WHO[a]		China[b]	
				limit ($\mu g\ L^{-1}$)	Exceedance rate (%)	limit ($\mu g\ L^{-1}$)	Exceedance rate (%)
As	92.3	1.71 ± 0.04	0.5–3.5	10	0.3	10	0.3
Cr	7.7	5.32 ± 0.73	4–389	50	1.7	50	1.7
Pb	30.1	4.23 ± 0.15	0.6–24	10	3.3	10	3.3
Cd	16.0	0.98 ± 0.05	0.3–14	3	4.3	5	2.4
Hg	46.1	0.03 ± 0.002	0.01–12	1	0	1	0
Cu	96.8	20.9 ± 2.4	2–348	3000	0	1000	0
Zn	98.3	72.1 ± 6.0	1–753	1000	0	1000	0

[a] WHO: Guidelines for drinking-water quality (WHO, 2017)
[b] China: Standards for drinking water quality (China MOH, 2006)

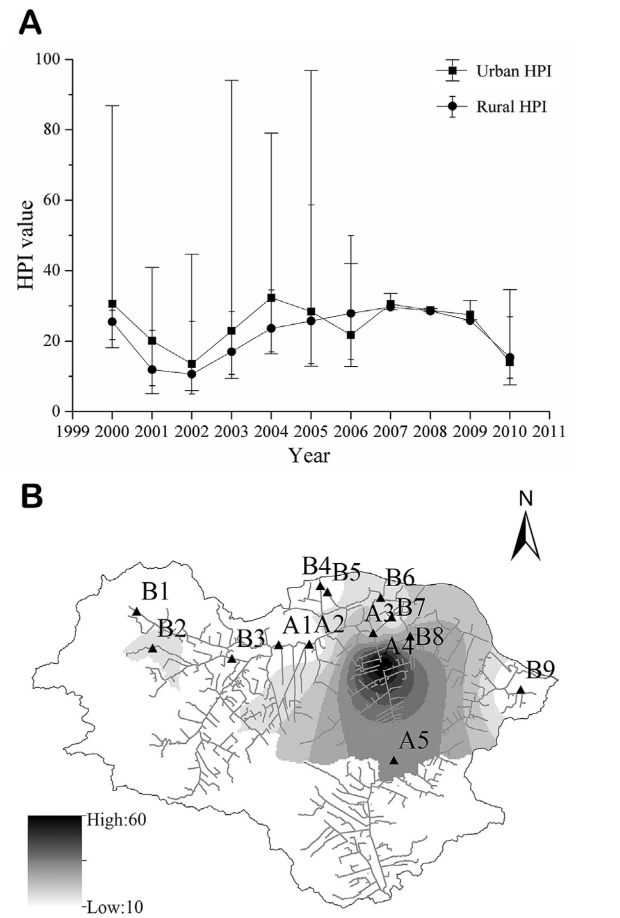

Fig. 3. (a) Temporal variation of HPI (Square/Round: Mean; Top line: Maxmium; Bottom line: Minimum), (b) Spatial distribution of HPI.

construction and increased sewage production associated with a rapidly expanding city population (Fig. 2a) (Mei et al., 2014). The distinct decline in the HPI in 2010 is predominantly due to a dilution effect resulting from abnormally high precipitation in 2010 (2782 mm vs an average annual 1767 mm).

Spatial analysis of HPI values in the Wen-Rui Tang River watershed identified that heavy metal pollution was most serious around monitoring site A4 (Fig. 3b). The A4 area was an old industrial area which lacks wastewater treatment facilities. In 2010, there were 119 electroplating plants and 11 leather factories that contributed heavy metals to the surrounding soil or by direct discharge into the river system; illegal discharges have been reported repeatedly (WEPB, 2014). The pollutants produced by electroplating factories were shown to accumulate in the river sediments where they are release to the water column over time (Liu et al., 2008).

Although the proportion of industrial land in sub-basin B9 was about 5-fold higher than B4, the HPI values were similar (Fig. 2b, Fig. 3b). This discrepancy reflects the effective wastewater treatment facilities associated with the high-tech industrial zone in the B9 sub-basin. While the A5 sub-basin had no industrial lands, it displayed relatively high HPI values (50–60) in 2005–2006. The high values at A5 reflect the downstream transport of heavy metals from the highly industrialized A4 sub-basin. These HPI vs land-use comparisons highlight the roles of wastewater treatment and riverine transport in affecting spatial patterns of heavy metals within watersheds. These results documented that effective wastewater treatment in industrialized areas can successfully protect downstream water quality. In contrast, heavy metal contamination of soil and river sediments can pose a long-term legacy effect within the immediate area as well as in downstream waterbodies.

3.3. Human health risk assessment

We used the hazard index (HI) to express the total potential health risk from heavy metals, which was the sum of hazard quotients (HQs) from all possible exposure pathways. The ingestion hazard quotient value (HQ_{in}) was far higher than dermal absorption (HQ_d) as typically found in the literature; therefore the HI values were approximately equal to HQ_{in} (Wu et al., 2009). The HI values estimated for residents in the Wen-Rui Tang River watershed are summarized in Table 3 for three time periods: Early: 2000–2003, Mid: 2004–2007, and Late: 2008–2010). The HI values for all heavy metals evaluated (As, Pb, Cd, Hg, Cu, Zn) were lower than the threshold value of concern, which we considered 1.0 in this study. Thus, the HI values suggest low risk for residents throughout the watershed. However, it is noteworthy that HI values for As were more than an order of magnitude higher than Pb, Cd, Zn and Cu, suggesting that human-health surveillance and environmental regulators should pay particular concern to As sources and exposure pathways in the watershed.

The HI values for As gradually declined over the study period for all monitoring sites. The higher risk areas were A1 (4.4×10^{-1}) and B5 (3.5×10^{-4}) (Figure 1). The HI for Pb increased at sites A3 (3.5×10^{-2}) and A4 (3.3×10^{-2}) in the central city in the late 2000s. In contrast, HI values for Pb increased at the other sites from 2000 to 2007 before declining through 2010. For Cd, the HI values for A5, B6, B7 and B8 increased in early and middle periods before decreasing in the late period. HI values at the remaining sites consistently increased, except for A4 which decreased after the mid-period. The highest risk site was A4 (1.1×10^{-2}) with a HI value about 10 times higher than the other sites in the early and middle periods. HI values for Hg showed small fluctuations over the study period; however, HI values were relatively low for the entire study period, except for B9 which reached a value of 8.6×10^{-4} in the early 2000s. The risk trends for Zn and Cu were not included in Table 3 because of the lack of long-term historical data for these metals. The highest risk sites for Cu were A4 (3.5×10^{-2}) and A5 (2.8×10^{-2}), while the highest risk site for Zn was B3 (1×10^{-3}) at the end of the study period.

The spatial distributions of carcinogenic risk (CR) values for As and Cd in the Wen-Rui Tang River watershed are shown in Figure 4. The cancer risk for As exceeded the acceptable range (10^{-4}) at most monitoring sites, especially in the pre-2004 period (Fig. 4a). These findings raise serious concerns for adverse carcinogenic effects from long-term exposure to arsenic throughout the watershed. The CR value gradually decreased to levels generally less than the 10^{-4} threshold value after 2004. Spatially, the highest risk areas were located in the central and northern areas of the city. The CR values for Cd were all within the acceptable range (10^{-4}~10^{-6}) (Fig. 4b). The CR temporal trend for Cd increased through 2007 before declining between 2007 and 2010. The highest risks were found in the areas surrounding A4 and A5.

Considering the combined results of the HI and CR indices, we summarize that the high risk regions for each metal in the Wen-Rui Tang River watershed are as follows: (1) As pollution was the major heavy metal for human-health concern and carcinogenic and non-carcinogenic risks were most prevalent in the northern urban area. (2) Cd risk was highest in the A4 (industrial zone) and downstream A5 area with the highest carcinogenic risk (3.4×10^{-5} and 2.3×10^{-5}) and non-carcinogenic risk (1.1×10^{-2} and 7.7×10^{-3}), respectively. (3) The high risk zones for Pb were around B3 and B6 (HI

Table 3
The hazard index (HI) in the Wen-Rui Tang River basin for various time periods.

Site	As			Pb			Cd			Hg			Cu	Zn
	Early[a]	Mid[b]	Late[c]	Early[a]	Mid[b]	Late[c]	Early[a]	Mid[b]	Late[c]	Early	Mid	Late	2009–2010	2009–2010
A1	4.4×10^{-1}	1.7×10^{-1}	1.3×10^{-1}	2.1×10^{-2}	3.4×10^{-2}	2.6×10^{-2}	9.3×10^{-4}	2.3×10^{-3}	2.9×10^{-3}	1.7×10^{-4}	1.9×10^{-4}	1.2×10^{-4}	1.6×10^{-2}	6.2×10^{-4}
A2	1.7×10^{-1}	1.5×10^{-1}	8.4×10^{-2}	3.3×10^{-2}	3.5×10^{-2}	2.8×10^{-2}	1.0×10^{-3}	2.0×10^{-3}	3.1×10^{-3}	1.8×10^{-4}	2.1×10^{-4}	1.0×10^{-4}	1.4×10^{-2}	5.5×10^{-4}
A3	2.7×10^{-1}	1.6×10^{-1}	1.5×10^{-1}	2.8×10^{-2}	3.0×10^{-2}	3.5×10^{-2}	2.6×10^{-3}	3.1×10^{-3}	3.2×10^{-3}	2.1×10^{-4}	2.1×10^{-4}	1.4×10^{-4}	1.5×10^{-2}	3.4×10^{-4}
A4	3×10^{-1}	1.5×10^{-1}	1.4×10^{-1}	2.3×10^{-2}	3.0×10^{-2}	3.3×10^{-2}	1.1×10^{-2}	1.1×10^{-2}	4.2×10^{-3}	1.9×10^{-4}	2.1×10^{-4}	1.0×10^{-4}	3.5×10^{-2}	3.2×10^{-4}
A5	2.2×10^{-1}	1.5×10^{-1}	1.5×10^{-1}	1.7×10^{-2}	2.8×10^{-2}	2.6×10^{-2}	2.3×10^{-3}	7.7×10^{-3}	4.3×10^{-3}	2.1×10^{-4}	2.1×10^{-4}	1.2×10^{-4}	2.8×10^{-2}	5.4×10^{-4}
B1	1.6×10^{-1}	1.1×10^{-1}	1.1×10^{-1}	2.7×10^{-2}	3.2×10^{-2}	2.8×10^{-2}	8.6×10^{-4}	2.4×10^{-3}	3.2×10^{-3}	1.6×10^{-4}	2.4×10^{-4}	1.2×10^{-4}	1.1×10^{-2}	5.3×10^{-4}
B2	2.8×10^{-1}	1.1×10^{-1}	9.2×10^{-2}	3.0×10^{-2}	3.5×10^{-2}	2.7×10^{-2}	1.8×10^{-3}	2.7×10^{-3}	3.2×10^{-3}	2.9×10^{-4}	3.0×10^{-4}	1.4×10^{-4}	1.0×10^{-2}	2.6×10^{-4}
B3	2×10^{-1}	1.5×10^{-1}	1.4×10^{-1}	2.0×10^{-2}	3.7×10^{-2}	2.6×10^{-2}	7.4×10^{-4}	2.3×10^{-3}	3.1×10^{-3}	2.0×10^{-4}	3.2×10^{-4}	1.4×10^{-4}	2.3×10^{-2}	1.0×10^{-3}
B4	2.4×10^{-1}	1.8×10^{-1}	1.6×10^{-1}	1.9×10^{-2}	3.3×10^{-2}	2.8×10^{-2}	8.9×10^{-4}	2.1×10^{-3}	2.9×10^{-3}	3.3×10^{-4}	1.5×10^{-4}	1.2×10^{-4}	1.4×10^{-2}	3.3×10^{-4}
B5	3.5×10^{-1}	2.2×10^{-1}	1.8×10^{-1}	2.6×10^{-2}	2.9×10^{-2}	2.2×10^{-2}	9.3×10^{-4}	2.4×10^{-3}	3.1×10^{-3}	3.5×10^{-4}	2.6×10^{-4}	1.3×10^{-4}	8.2×10^{-3}	2.6×10^{-4}
B6	2.6×10^{-1}	1.8×10^{-1}	1.7×10^{-1}	3.9×10^{-2}	3.7×10^{-2}	2.4×10^{-2}	1.2×10^{-3}	3.0×10^{-3}	2.9×10^{-3}	1.5×10^{-4}	2.7×10^{-4}	1.3×10^{-2}	1.4×10^{-2}	4.2×10^{-4}
B7	2.1×10^{-1}	1.7×10^{-1}	1.4×10^{-1}	2.2×10^{-2}	3.0×10^{-2}	2.2×10^{-2}	8.1×10^{-4}	3.5×10^{-3}	2.9×10^{-3}	1.3×10^{-4}	1.8×10^{-4}	1.1×10^{-4}	1.5×10^{-2}	2.8×10^{-4}
B8	1.9×10^{-1}	1.5×10^{-1}	1.5×10^{-1}	2.4×10^{-2}	2.7×10^{-2}	2.2×10^{-2}	1.7×10^{-3}	6.2×10^{-3}	3.4×10^{-3}	1.7×10^{-4}	1.4×10^{-4}	1.2×10^{-4}	1.9×10^{-2}	3.0×10^{-4}
B9	2.3×10^{-1}	1.3×10^{-1}	1.4×10^{-1}	2.5×10^{-2}	3.4×10^{-2}	2.7×10^{-2}	6.7×10^{-4}	1.9×10^{-3}	3.0×10^{-3}	8.6×10^{-4}	2.7×10^{-4}	1.1×10^{-4}	1.8×10^{-2}	4.4×10^{-4}

[a] Early: 2000–2003.
[b] Mid: 2004–2007.
[c] Late: 2008–2010.

values > 3.7×10^{-2}) and A3 and A4 (non-carcinogenic risk ~3.4×10^{-2}). (4) High risk areas for Zn were around A4 (3.5×10^{-2}) and A5 (2.8×10^{-2}). (5) The high risk area for Cu was surrounding B3 (1×10^{-3}). (6) The entire watershed had low Hg risks (<1×10^{-3}). Examining the watershed as a whole, the city center area (A3, A4, B6) and immediate downstream site (A5) had the highest potential health risks from heavy metals reflecting the higher industrial capacity in this region.

Based on the sensitivity analysis results (section 3.4), metal concentration was the main factor influencing all types of health risk (contribution > 80%), while ingestion rate and body weight also contributed to the final health risk. Therefore, the higher health risk is largely associated with the higher pollutant loads discharged from wastewater in these zones. Notably for site A5, people in the rural region have higher ingestion rate and lighter body weight which contributed to high risk. High pollutant concentration contribution to health risk also explains the "hotspot" for CR-Cd at A4 where electroplating and leather factories are spatially concentrated. Overall, sites in rural areas showed lower potential health risks due to lower pollutant levels, but were appreciably higher than would be expected from exposure to natural (background) exposure levels. Although HPI increased from 2004 to 2007, As concentrations decreased constantly over the entire study period resulting in reduced cancer risk from As. The high cancer risk associated with Cd in 2004–2007 was caused by increased Cd release in untreated wastewaters, which were not efficiently collected for treatment during this time period. Strong regulatory actions, such as demolition of illegal factories along the river, sewage collection and treatment, and removal of river sediments, have been adopted to reduce current heavy metal emissions to the environment over the study period. However, there is still a strong legacy effect from past heavy metal emissions resulting in a time lag effect in observing decreased metal concentrations and reduced health risks.

3.4. Uncertainty in health risk assessment

There are a large number of uncertainties associated with the estimation of heavy metal health risk metrics. To provide a quantitative determination of uncertainty, we used Monte Carlo simulation to assess the risk probability range for the HI and CR assessment indices. Monte Carlo simulation results indicated the HI values for all sites fell within a relatively narrow range (Fig. 5a) and all distributions were below the critical HI value of 1.0. In contrast, the distribution of CR values for As exceeded the critical threshold of 10^{-4} for all sites. The exceedance rates ranged from a low of 4.1% at B1 to a high of 55.7% at B5. The CR range for Cd also showed a rare exceedance of the threshold value for site A4 with an exceedance rate of 2.6% (Figure. 5b). The results of the sensitivity analysis (Table 4) assessed the importance of five factors contributing to health risk. The most sensitive factor was C_i (86.3–97%) for all metals, with much smaller contributions from IR (0.4–3.8%), BW (0.7–3.3%), ED (0.6–3.4%) and (0.7–3.5%). The hazard index (Cu and Zn) and CR-Cd were more sensitive to metal concentrations than for the other metals (~10%).

While the overall quantitative assessment did not show potential cancer risk for As and Cd at some monitoring sites according to the water sample concentrations, the Monte Carlo simulation results assigned a probability to the potential risk. The Monte Carlo approach takes into account variable exposure times, ingestion rates and pollutant concentrations in determining the probability. These results suggest that uncertainty analysis can remedy some deficiencies of the standard assessment methodologies, such as the loss of information from cross-sectional studies due to the lack of data for certain time periods (Gonzalez et al., 2005). Sensitivity

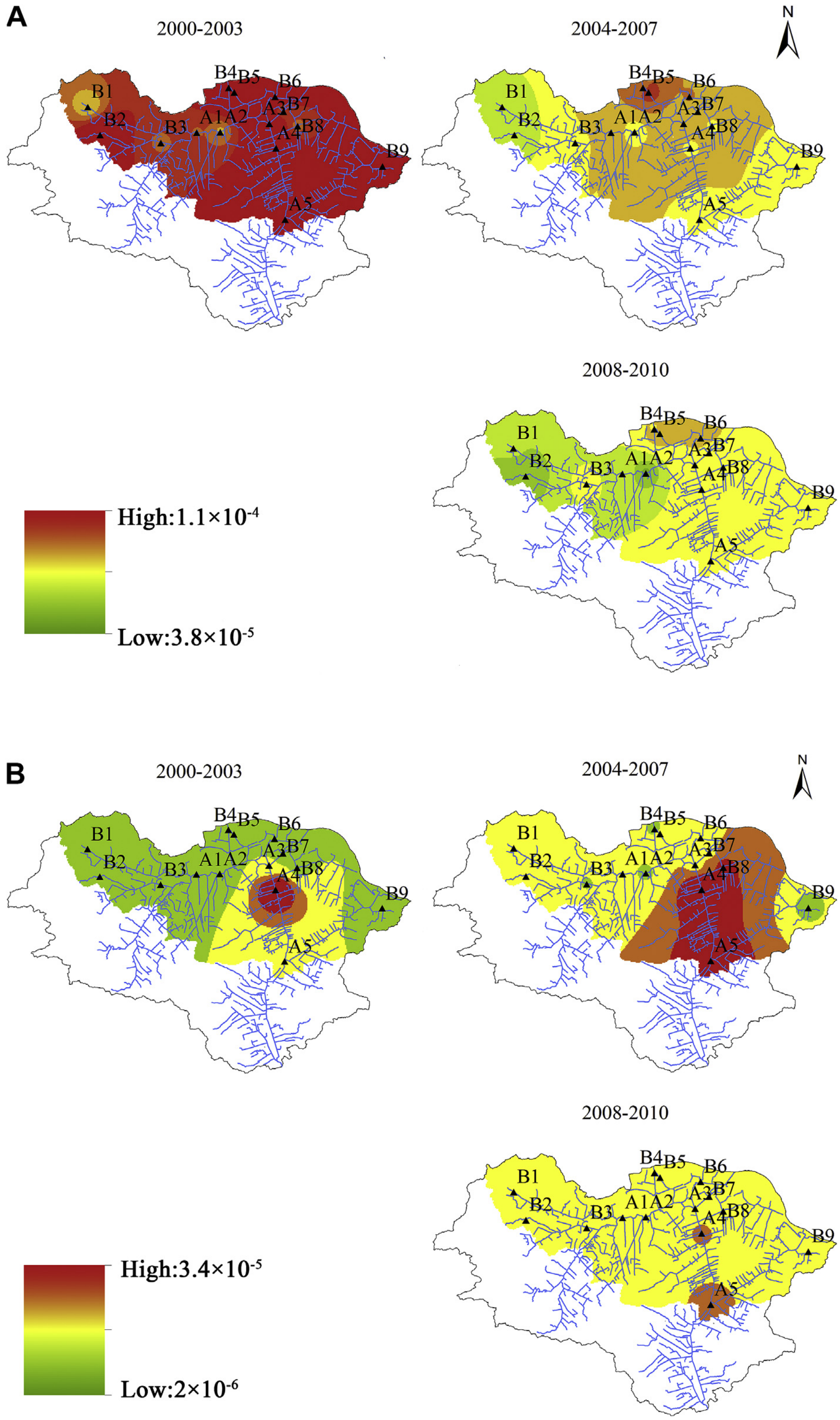

Fig. 4. CR for (a) As; and, (b) Cd.

analysis showed that most important factor for both HI and CR metrics was heavy metal concentration. Only control and management of pollutant discharge can reduce the threat of elevated heavy metal concentrations in aquatic environments. The much higher sensitivity weightings for HI-Zn and HI-Cu versus Cd to health risk were caused by different factors. The elevated uncertainty associated with HI-Cu and HI-Cu was caused by a smaller data set that reduced the efficiency for fitting the concentration distribution and subsequently reduced the simulation accuracy. In contrast, Cd had low detection rates and non-detectable concentrations were replaced by the detection limit value that conservatively reduced the accuracy of the simulation. Therefore,

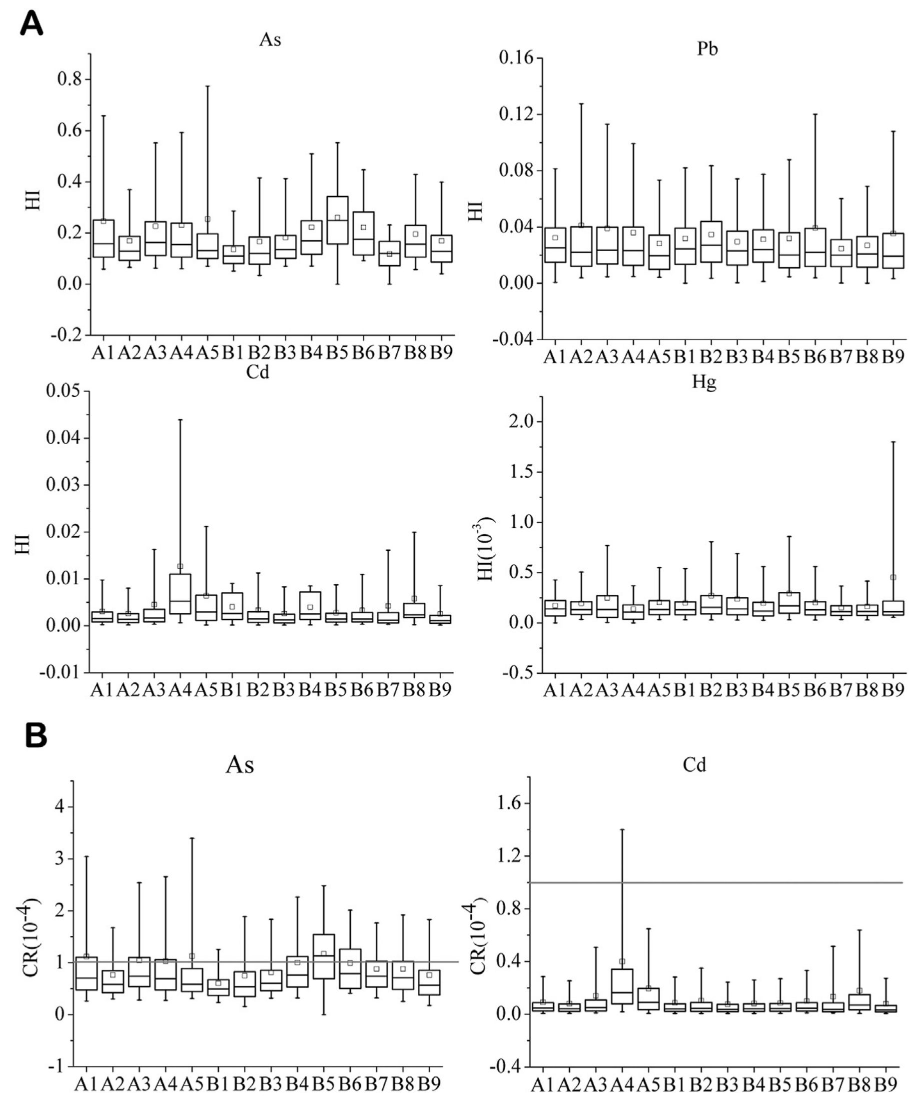

Fig. 5. (a) HI range for As, Pb, Cd and Hg; and, (b) CR range for As and Cd (Black line is the critical value (1×10^{-4})).

Table 4
Sensitivity analysis of health risk factors.

	Sensitivity factor				
	Concentration (C_i)	Ingestion rate (IR)	Body Weight (BW)	Exposure duration (ED)	Average time (AT)
HI-As	87.0%	3.2%	2.9%	3.4%	3.5%
HI-Pb	86.3%	3.8%	3.3%	3.1%	3.4%
HI-Cd	96.8%	0.8%	1.0%	0.6%	0.8%
HI-Hg	87.7%	3.0%	3.3%	3.0%	3.1%
HI-Cu	97.0%	0.4%	0.9%	1.0%	0.7%
HI-Zn	96.8%	1.0%	0.7%	0.8%	0.7%
CR-As	86.8%	3.3%	3.2%	3.3%	3.4%
CR-Cd	96.6%	0.7%	1.0%	0.7%	0.9%

larger data sets and enhanced analytical detection limits are two approaches for reducing uncertainty in health risk assessment analyses.

The combined results of the quantitative indices and uncertainty analysis clearly point to a potential health risk from As in many areas within the Wen-Rui Tang River watershed. Given the potential health hazard associated with As, special attention is warranted for As regulatory/remediation actions and cancer surveillance observations in the Wen-Rui Tang River watershed. Similarly, our analysis identified a potential human health risk from Cd contamination in the industrial area surrounding the A4 site which merits further investigation.

4. Summary and conclusions

Although concentrations of As, Pb, Cr and Cd sometimes exceeded the permissible limits for drinking water set by WHO and China MOH for some sites, metal concentrations were below limits suggested to impose ecological risk at all monitoring sites in the Wen-Rui Tang River watershed. The temporal trend in HPI values showed a decrease before 2002, an increase between 2002 and 2007, and a sustained decrease after 2007 indicating that recent regulatory and remediation activities are successfully decreasing metal concentrations in surface waters. The relatively high pollution levels around industrial sites were consistent with current and historical release trends of industrial wastes associated with the electroplating and leather tanning industries that are concentrated in these areas.

Combining the human health risk assessment with Monte Carlo uncertainty analysis provided a more effectively evaluation of the potential risk of heavy metal exposure to human health. The health risk was most sensitive to heavy metal concentrations. Overall, there was low potential for non-carcinogenic human health risks. In contrast, there was a prominent potential carcinogenic risk from As at urban sites as opposed to rural sites. Based on the Monte Carlo uncertainty analysis, cancer risk from As existed at all sites when taking uncertainty bounds into account. Similarly, a potential cancer risk from Cd was identified at the industrial pollution hotspot, but fortunately this risk declined over the time period of this study. The uncertainty assessment identified the importance of comprehensive pollutant data sets and enhanced analytical pollutant detection accuracy to decrease the uncertainty of health risk analysis. This study provides guidance for surface water heavy metal regulatory activities and public health surveillance actions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.02.020.

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