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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,