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Authors

Xia, Fang
Qu, Liyin
Wang, Ting
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Distribution and source analysis of heavy metal pollutants in sediments of a rapid developing urban river system

Fang Xia^a, Liyin Qu^a, Ting Wang^a, Lili Luo^a, Han Chen^a, Randy A. Dahlgren^{a, b}, Minghua Zhang^{a, b}, Kun Mei^{a, **}, Hong Huang^{a, *}

^a Key Laboratory of Watershed Environmental Science and Health of Zhejiang Province, Southern Zhejiang Water Research Institute (iWATER), Wenzhou Medical University, China

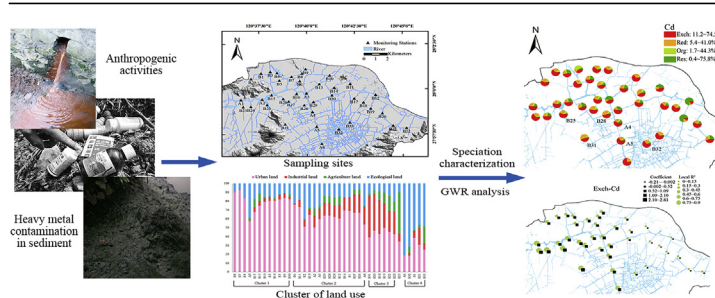
^b Department of Land, Air and Water Resources, University of California, Davis, USA



HIGHLIGHTS

- Sediments in Wenrui Tang River were seriously contaminated with heavy metals.
- Some heavy metals possibly derived from similar pollution source.
- Correlation of the heavy metal speciation with land use type was analyzed.
- GWR showed heavy metal pollution mainly associated with industrial activities.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metal pollution of aquatic environments in rapidly developing industrial regions is of considerable global concern due to its potential to cause serious harm to aquatic ecosystems and human health. This study assessed heavy metal contamination of sediments in a highly industrialized urban watershed of eastern China containing several historically unregulated manufacturing enterprises. Total concentrations and solid-phase fractionation of Cu, Zn, Pb, Cr and Cd were investigated for 39 river sediments using multivariate statistical analysis and geographically weighted regression (GWR) methods to quantitatively examine the relationship between land use and heavy metal pollution at the watershed scale. Results showed distinct spatial patterns of heavy metal contamination within the watershed, such as higher concentrations of Zn, Pb and Cd in the southwest and higher Cu concentration in the east, indicating links to specific pollution sources within the watershed. Correlation and PCA analyses revealed that Zn, Pb and Cd were dominantly contributed by anthropogenic activities; Cu originated from both industrial and agricultural sources; and Cr has been altered by recent pollution control strategies. The GWR model indicated that several heavy metal fractions were strongly correlated with industrial land proportion and this correlation varied with the level of industrialization as demonstrated by variations in

* Corresponding author. Key Laboratory of Watershed Environmental Science and Health of Zhejiang Province, Southern Zhejiang Water Research Institute (iWATER), Wenzhou Medical University, Wenzhou, 325035, China.

** Corresponding author. Key Laboratory of Watershed Environmental Science and Health of Zhejiang Province, Southern Zhejiang Water Research Institute (iWATER), Wenzhou Medical University, Wenzhou, 325035, China.

E-mail addresses: meikun@iwaterlab.com (K. Mei), huanghongpanda@163.com (H. Huang).

local GWR R^2 values. This study provides important information for assessing heavy metal contaminated areas, identifying heavy metal pollutant sources, and developing regional-scale remediation strategies.
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1. Introduction

Heavy metal pollution in aquatic environments has the potential to cause serious aquatic ecosystem and human health impairments (Chowdhury et al., 2016). Metals dissolved in natural waters are easily absorbed by aquatic organisms and can rapidly bioaccumulate/biomagnify within the aquatic food web. Chronic metal exposure in aquatic ecosystems may adversely affect the activity, growth, metabolism, and reproduction of aquatic organisms (Wright and Welbourn, 2002). Long-term exposure to heavy metals by humans has been implicated in causing intellectual and developmental disabilities, behavioral problems, hearing loss, learning and attention problems, disruption of visual and motor function, and various cancers (Sarkar, 2009; Lanphear et al., 2005; Adams et al., 2014). A significant source of heavy metals in the human diet may originate from higher trophic level aquatic organisms (e.g., predatory fish) providing a linkage between aquatic food webs and human health. Further, interactions associated with chronic exposure to multiple heavy metals may induce more severe ecosystem and human health consequences than might be expected from low individual metal concentrations alone. Thus, it is important to fully assess the suite of heavy metals as well as their solid-phase fractionation to fully assess the toxicological risks associated with heavy metals in the environment.

The adverse impact of heavy metal pollution on aquatic ecosystems is especially severe in areas experiencing rapid urbanization and industrialization (Pan and Wang, 2012). Sediments can either release metals directly to the water column or serve as the source of metals for bioaccumulation/biomagnification in aquatic organisms, such as benthic fauna, shrimp and fish (Goretti et al., 2016). Anthropogenic activities are the primary contributor of heavy metal pollutants to sediments and soil (Wong et al., 2017) and therefore heavy metal pollution is strongly linked to land use (Li et al., 2017a, b). For example, heavy metals become enriched in paddy fields due to chemical fertilizers, animal wastes, atmospheric deposition and wastewater discharge (Chen et al., 2012; Li et al., 2017a, b). Pollutants discharged into receiving waters directly or carried by runoff will finally accumulate in aquatic sediments. Therefore, investigating the distribution and speciation of metals from contrasting land uses may provide unique chemical signatures in aquatic sediments that in turn provide a scientific basis to assess the pollutant source and their potential ecological and human health risks. The assessment of potential metal risks depends not only on total metal concentrations, but also on their chemical forms (i.e., speciation) influencing bioaccessibility and bioavailability (Simpson et al., 2012). For example, the exchangeable and weak acid extractable fractions are considered as the most mobile and bioavailable metal fractions (Tessier et al., 1979; Pueyo et al., 2008). Sediment characteristics (e.g., organic matter, redox status and pH) have a strong effect on distribution of metal fractions and their bioavailability, such as the positive correlation observed between organic matter and the oxidizable fraction of Cu and Pb in Tasik Chini, Malaysia (Ebrahimpour and Mushrifah, 2008). Thus, multi-step sequential extraction schemes have been used to estimate the bioavailability of metals in sediments and their potential risk to aquatic ecosystems and humans (Sakan et al., 2016).

Spatial analysis provides an advantage of understanding the

variation of several impact factors on heavy metal pollution and generally involves the analysis of relationships among impact factors from a given geographic location. However, the relationship or structure of the variables will change within a watershed, the so called “spatial non-stationarity” condition (McMillen, 2004). Traditional regression models, such as ordinary least squares models (OLS model), assume a stable relationship between the independent and dependent variables throughout the study area, resulting in a uniform regression coefficient for the entire study region and failure to consider any variation of spatial characteristics (Williams et al., 2005).

Geographically weighted regression (GWR) was developed to overcome these disadvantages of traditional regression models. GWR is efficient for handling the spatial variation in the relationship between variables. In GWR models, the site location is considered in the regression equation to build the relationship between the independent and dependent variables when non-stationarity of spatial relationships exists (Fotheringham et al., 2002). This approach has been widely employed in water pollution management and aids in contamination prediction and risk assessment. For example, GWR was used for spatial prediction of trace metal concentrations in surface and ground waters based on spatial predictors in Pakistan, and the associated health risks of these waters were estimated according to the predicted spatial metal concentrations (Bhowmik et al., 2015). Similarly, Tu, 2013 demonstrated improvement of GWR models for predicting the influence of land use on water quality at the watershed scale in Northern Georgia compared to least squares regression. Additionally, Wu et al. (2016) applied GWR to identify the spatially varying relationship between land-use types and total heavy metal concentrations in sediment, but did not assess the relationship with heavy metal speciation. Thus, there is a research gap in studies using GWR methods to coupling land-use types with speciation of heavy metals in sediments, which is fundamental knowledge required for remediation and mitigation of heavy metal pollutants at the watershed scale. Therefore, this paper is novel in utilizing GWR to assess relationships between land-use types and heavy metal concentrations and their corresponding chemical fractionation, with the consideration of their spatial variation.

Given the importance of aquatic ecosystem protection and the negative impacts of heavy metal pollution on human health, new spatial analysis tools are highly warranted, especially in rapidly developing regions with a large number of industrial enterprises involving heavy metals. The main purposes of this study were to (i) assess heavy metal contamination of sediments in a highly polluted river systems affected by rapid industrialization, (ii) identify spatial distribution of total metal concentrations and solid-phase metal fractions at the watershed scale, and (iii) combine GWR with traditional multivariate statistical analysis to investigate variation in relationships between anthropogenic activities and heavy metals in river sediments. This study provides a framework for spatial assessment of metal pollution sources and information to guide remediation at the watershed scale. Further, this study highlights the power of incorporating GWR models in sediment pollution assessments and its potential for widespread use in studies of environmental pollution.

2. Material and methods

2.1. Study area

The Wen-Rui Tang River watershed is located in rapidly industrializing Wenzhou, Zhejiang province of eastern China (Fig. 1). The river originates from Lishui Mountain streams and flows ~34 km to the East China Sea, covering a drainage area of 740 km² with ~370 km² within the urban center (Chen et al., 2016). The basin has an average annual temperature of 18 °C and average annual rainfall of 1695 mm with ~70% of precipitation falling between April to September. The basin has a population of ~9.2 million with large variations in population density from rural areas to the urban center. The Wen-Rui Tang River plays important watershed roles in irrigation, aquaculture, drainage and water supply. Wenzhou is representative of economic development in eastern China with small workshops and older factories making a large contribution to the local economy. This industrial structure contributed large volumes of untreated wastewaters and waste residues directly to the river system due to the absence of effective management and legislative regulations over the development period.

A previous study examining non-metal water quality conditions in this watershed used data from 52 sampling sites that were divided into corresponding sub-catchments (Chen et al., 2016). In this study, land use was divided into four categories: i) urban lands including residential, commercial and transportation lands, ii) industrial lands representing industrial and mining lands, iii) agriculture lands, and iv) non-managed ecological lands including barren land and water areas (Fig. S1).

2.2. Sediment sampling and analytical methods

A total of 39 surface sediment samples (0–10 cm) were collected by grab bucket sampler across the watershed from the mid-channel of the Wen-Rui Tang River and its tributaries in March 2017 (Fig. 1). A GPS was used to record geographic information (World Geodetic System-1984 coordinate system) for each sampling site. At each site, three surface sediments were collected and composited to obtain a single sample for analysis (Ke et al., 2017). Samples were sealed in clean polyethylene bags and transferred to the laboratory for immediate storage in a cryogenic freezer (−80 °C). Samples

were freeze-dried and ground to pass a 150-mesh screen (Wang et al., 2010). All samples were quartered to provide representative sub-samples for further physicochemical analysis.

Each sample was digested with mixed acids (HNO₃-HCl-HF-HClO₄) to obtain total metal concentrations. The modified BCR sequential extraction procedure was used to chemically speciate metals into operationally-defined exchangeable, reducible, organic bound and residual fractions (Quevauviller et al., 1997). The extraction procedure was as follows: (1) Acid exchangeable fraction (Exch) was extracted by 0.1 M HOAc; (2) Reducible fraction (Red) was extracted by 0.5 M NH₄OH·HCl; (3) Organic bound fraction (Org) was extracted by 30% H₂O₂ (pH = 2–3) and 1 M NH₄OAc; and (4) Residual fraction (Res) was determined using the mixed acid (HNO₃-HCl-HF-HClO₄) digestion. Detailed information for the BCR procedure is provided in Table S1 (Wang et al., 2017). With respect to the BCR method, the exchangeable fraction was considered as the bioavailable fraction (Bielicka-Giełdoń et al., 2013; Rosado et al., 2016). Concentrations of Cu and Zn were determined by atomic absorption spectrometry (PinaAcle 900, Perkin Elmer; detection limit, Cu = 0.01, Zn = 0.01 mg L⁻¹) and Pb, Cd, and Cr were quantified by inductively coupled plasma mass spectrometry (Agilent 8800 ICP-MS, Agilent Technologies; detection limit, Pb = 0.005, Cd = 0.01, Cr = 0.1 mg L⁻¹). The detection limit was calculated as 3 times the standard deviation of blank samples (Pourreza and Ghanemi, 2009). All samples were analyzed in duplicate and the relative standard deviation (RSD) of all duplicate samples was ±5%. The GBW-07312 reference sediment (Chinese Academy of Geological Sciences) was used for quality control and we achieved recoveries for total metal concentrations of 89–107%. The average pH value for sediment samples was 7.1, ranging from 6.6 to 7.9 (water, m:v = 1:5). Average organic carbon content was 36.7 g kg⁻¹, ranging from 7.8 to 90.4 g kg⁻¹ (potassium dichromate oxidation method; Lu, 2000). All plastic and glass vessels were soaked in dilute HNO₃ (v/v = 1/5) for at least 24 h, and thoroughly rinsed with 18 MΩ de-ionized water prior to use.

2.3. Assessment of heavy metal pollution

The geoaccumulation index (I_{geo}) developed by Müller (1979) was used in this study to evaluate the contamination degree of heavy metals in sediment. I_{geo} was calculated as follow:

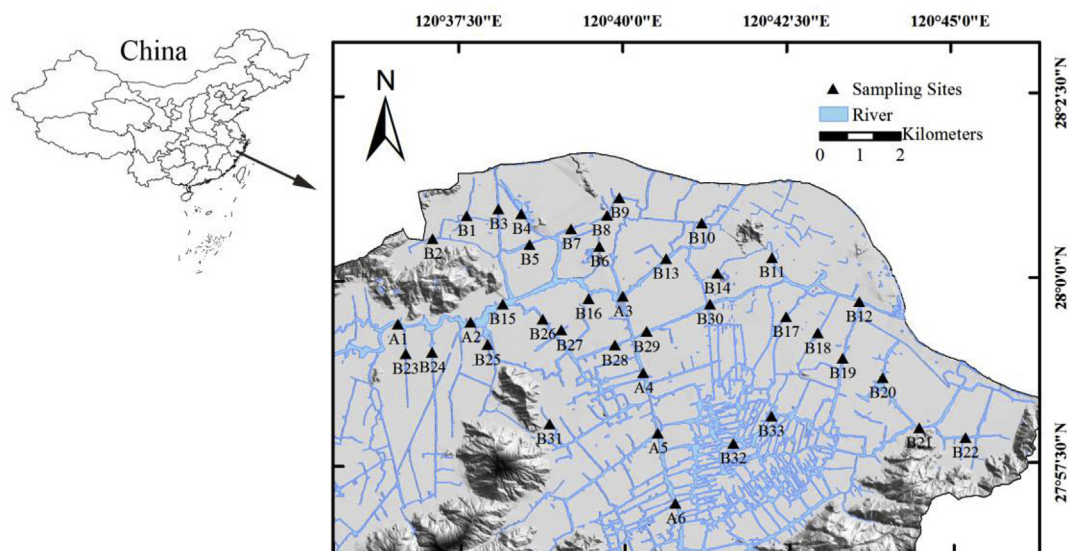


Fig. 1. Location of sampling sites in the study region.

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right)$$

where C_n and B_n are the concentration of metal n in the sample and background, respectively. Variation of background concentrations is corrected using a multiplier value of 1.5 for B_n .

Seven classes were identified according to I_{geo} values: $I_{geo} < 0$, Class 0, practically uncontaminated; $0 < I_{geo} < 1$, Class 1, uncontaminated to moderately contaminated; $1 < I_{geo} < 2$, Class 2, moderately contaminated; $2 < I_{geo} < 3$, Class 3, moderately contaminated to heavily contaminated; $3 < I_{geo} < 4$, Class 4, heavily contaminated; $4 < I_{geo} < 5$, Class 5, heavily contaminated to extremely contaminated; and $I_{geo} > 5$, Class 6, extremely contaminated.

2.4. Geographically weighted regression (GWR)

As an optimized spatial analysis method, GWR is a powerful tool for exploring the spatial relationship between variables by establishing the local regression equation for each spatial location. The GWR model was defined as follows:

$$Y_j = \beta_0(u_j, v_j) + \sum_{i=1}^p \beta_i(u_j, v_j) X_{ij} + \varepsilon_j \quad (1)$$

where (u_j, v_j) represents the coordinate for location j , β_0 represents the regression intercept for point j , X_{ij} represents the independent variable i for the j th point, β_i represents the regression coefficient, and ε_j represents the residual error for the j th point.

This GWR model merges the dependent variables and explanatory variables for any point that falls within the bandwidth of each target element. If the bandwidth is too small, it will contain too few data points and if it is too large, it will conceal the local heterogeneity. The shape and size of the bandwidth depends on the kernel type, bandwidth method, the distance, and the parameters for the adjacent points (McMillen, 2004). In order to optimize the spatial weighting function, we applied a gauss function method as follows:

$$W_{ij} = \exp \left[- \left(\frac{d_{ij}}{b} \right)^2 \right] \quad (2)$$

where d_{ij} represents the distance between point i and point j , and b represents the kernel bandwidth. ArcGIS 10.2 was used to examine both fixed and adaptive bandwidths (Tu and Xia, 2008). Based on the sampling site distribution in the watershed and preliminary analysis, we chose the fixed bandwidth for the GWR model.

A stepwise regression model was employed to explore relationships between independent variables (land-use types) and heavy metal concentrations. The regression coefficient (R^2) was optimized by manually adding or subtracting variables to avoid multicollinearity. In addition, cluster, PCA and correlation analyses were conducted with SPSS (ver. 20.0) before GWR to explore relationships between heavy metal concentrations and land use. For cluster analysis, the 39 sampling sites were grouped into four clusters based on land-use type percentage using Squared Euclidean Distance. PCA analysis extracted three principle components that explained 75.9% of total variance.

3. Results

3.1. Cluster analysis of sampling sites

Spatial cluster analysis was performed to better understand

heavy metal distribution in the Wen-Rui Tang River watershed. The 39 sampling sites were grouped into four clusters and are displayed with their corresponding land-use characterization in Fig. S1. Cluster 1 was dominated by urban lands (79.4%) in the city center. Cluster 2 averaged 63.3% urban and 13.0% industrial lands and was mainly located along the periphery of the city center. Cluster 3 had the highest proportion of industrial lands (up to 33.1%) and contained two types of industrial districts in suburban areas, a new industrial region in the east and an older, traditional industrial park in the southwest. While site B22 in Cluster 3 had a high proportion of industrial land (23.9%), it was notable in having low heavy metal concentrations. Cluster 4 sampling sites were mainly located in areas having a high proportion of wetlands and wildlands (47.0–81.2%), which we called ecological lands. Finally, Site B23 having 46.1% agricultural land use did not group into any of the four clusters.

3.2. Heavy metal concentrations in Wen-Rui Tang River sediments

Concentrations of total and speciation metal fractions for five metals in Wen-Rui Tang River sediments are summarized in Table 1. Average total concentrations of Cu, Zn, Pb, Cd and Cr were 310, 1362, 115, 17.7 and 193 mg kg⁻¹, respectively. Compared to local background concentrations (Wang et al., 2007), metal concentrations were considerably elevated: Cr ~2 ×, Pb ~3 ×, Cu and Zn ~10 ×, and Cd ~100 × time higher than background levels. In addition, heavy metal concentrations generally exceeded the SQG standard (Smith et al., 1996), which identifies a potential risk for aquatic organisms. According to calculation of I_{geo} , heavy metals in the study region accumulated in varying degrees. The Pb and Cr posed uncontaminated to moderately contaminated status; Cu was identified as moderately contaminated; Zn showed moderate to heavy contamination; and Cd was categorized as heavily contaminated in the study region. Metal concentrations in the Wen-Rui Tang River sediments were also elevated compared to several other rivers and lakes locally and globally (Table S2): Cu 3–14 ×, Zn 4–36 ×, Pb 1.1–10 × times, and Cd 4–880 × times higher than the concentrations in these other watersheds. Heavy metal contaminations in river sediments were much severer than that in Congo, which was identified with slight heavy metal pollution (Mwanamoki et al., 2014; Kilunga et al., 2017). In contrast, Cr concentrations were at levels similar to sediments from Dong Ting Lake (China), Yangtze River (China) and Red River (Vietnam), but 20 times higher than that in the Sinú River (Colombia). Overall, sediments in the Wen-Rui Tang River were highly contaminated by heavy metals, especially Cd and Zn.

BCR fractionation analysis showed that Org-Cu was the predominant Cu fraction (average - mg kg⁻¹): Org-Cu (170) > Res-Cu (41.6) > Exch-Cu (33.2) > Red-Cu (10.1). The Exch-Zn fraction, considered the most labile fraction and an indicator for environmental and human-health risk, contributed more than 50% of the total Zn content (average - mg kg⁻¹): Exch-Zn (932) > Red-Zn (355) > Org-Zn (243) > Res-Zn (90). The fractionation distribution of Cd was similar to Zn and dominated by the exchangeable fraction (average - mg kg⁻¹): Exch-Cd (10.0) > Red-Cd (6.3) > Org-Cd (1.8) ≈ Res-Cd (1.8). Lead and Cr fractions were both dominated by the residual fraction. Overall Pb fractionation followed (average - mg kg⁻¹): Res-Pb (49.0) > Org-Pb (32.6) ≈ Red-Pb (30.8) > Exch-Pb (5.7). Chromium fractionation followed (average - mg kg⁻¹): Res-Cr (117) > Org-Cr (75.1) > Red-Cr (4.7) > Exch-Cr (2.2). Correlation analysis generally indicated a significant positive correlation between organic bounded fractions and organic matter content due to the strong complexation with organic materials, except for Cr (Strawn and Sparks, 2000; Gao et al., 2015). In contrast, pH did not show any significant relationships with the various heavy metal

Table 1
Statistics for heavy metals in sediment (mg kg⁻¹).

	Mean	Max	Min	CV (%)	Background Value (Wang et al., 2007)	SQG (Smith et al., 1996)
Exch-Cu	33.1	320	0.42	122		
Red-Cu	10.1	56.6	2.22	89.3		
Org-Cu	170	2741	9.78	253		
Res-Cu	41.6	240	1.88	95.9		
T-Cu	310	5093	29.5	256	32.7	18.7
I _{geo} -Cu	1.7	6.7	-0.7			
Exch-Zn	932	5273	65.0	123		
Red-Zn	355	2488	35.0	126		
Org-Zn	243	1205	34.2	92.7		
Res-Zn	90.1	285	35.7	45.3		
T-Zn	1362	7616	263	107	109	124
I _{geo} -Zn	2.5	5.5	0.7			
Exch-Pb	5.7	110	0.58	30.0		
Red-Pb	30.8	296	6.69	151		
Org-Pb	32.6	139	7.91	87.9		
Res-Pb	49	149	8.25	73.7		
T-Pb	115	644	34.5	91.5	38.4	30.2
I _{geo} -Pb	0.7	3.5	-0.7			
Exch-Cd	9.95	135	0.11	251		
Red-Cd	6.31	129	0.05	345		
Org-Cd	1.78	32.9	0.03	314		
Res-Cd	1.83	16.8	0.01	206		
T-Cd	17.7	314	0.34	300	0.17	0.68
I _{geo} -Cd	3.7	10.3	0.4			
Exch-Cr	2.22	5.46	0.44	58.9		
Red-Cr	4.70	12.5	1.06	57.2		
Org-Cr	75.1	374	9.69	90.1		
Res-Cr	117	256	53.3	37.6		
T-Cr	193	440	94.2	39.6	88.1	52.3
I _{geo} -Cr	0.4	1.7	-0.4			

SQG, sediment quality guideline.

fractions (Table S4).

3.3. Watershed distribution of heavy metals in sediments

The spatial distribution of total metal concentrations in sediments displayed some similarities and differences among metals (Fig. 2). Zinc, Pb and Cd presented similar spatial distributions with a 'hot spot' in the southwest and generally decreasing concentrations from southwest to northeast in the watershed. Cadmium had larger spatial variation, as measured by the CV%, than that of Zn and Pb. The spatial distribution of the dominant metal fractions displayed contrasting patterns across the study area (Fig. S2). Spatial variation of Exch-Zn was similar to total Zn concentration with the most polluted area in the southwest. The concentration of Res-Pb in northern sites was higher than that in southern sites, and those in the east were greater than those in the west. Exch-Cd was detected at high concentrations for most sampling sites within the Wen-Rui Tang River watershed. The highest concentrations of Cr were identified in the eastern sites (except for B22) and decreased to the west; Cr showed the smallest spatial variation among the five metals (CV 39.6%). Res-Cr was identified as the dominant Cr species for most sites and displayed a spatial distribution similar to Res-Pb. Generally, southwestern sites had the highest Org-Cu concentrations and concentrations decreased to the northeast, except for B18, which appeared as an isolated 'hot spot'.

3.4. Heavy metals source analysis

Correlation analysis among heavy metals in surface sediments showed significant positive correlations among Zn, Pb and Cd indicating the potential for a similar pollution source (Table S3). Copper was significantly correlated with the other four metals, while Cr was only significantly correlated with Cu. This suggests

that the source of Cr may differ from that of the other metals. In addition, Cu, Zn and Pb were significantly correlated with organic, which might to the strong complexation of these matters to organic materials.

Principle Component Analysis (PCA) provided further information to distinguish possible sources of heavy metals in the study area. The first three components contributed 75.9% to the total variation (Table 2). PC1 explained 47.9% of the total variance with Exch-Zn, Exch-Pb, Exch-Cd, Red-Zn, Red-Pb, Red-Cd, Org-Zn, Org-Pb, Org-Cd, Red-Zn and Red-Cd contributing the most to explain the variation. In accordance with the correlation analysis, PCA results indicate that the various metal fractions may share a common source. A previous study concluded that Zn, Pb and Cu pollution in river systems was primarily impacted by similar anthropogenic activities (Qiao et al., 2013). Therefore, PC1 might represent an anthropogenic source contribution. PC2 explained 14.2% of the total variance with Exch-Cu, Org-Cu and Res-Cu having the highest loading weight. Copper is widely used in anthropogenic activities, including both industrial and agricultural production (Liu et al., 2007), thus PC2 was assumed to result from multiple sources of Cu pollution. PC3 explained 13.8% of the total variance with Cr showing higher loading values, which might indicate a distinctly different source of Cr pollution in the Wen-Rui Tang River watershed.

3.5. GWR analysis of relationships between land use and metal speciation

Stepwise regression indicated significant relationships between various metal fractions and land-use proportions (Table 3). Except for Res-Pb, all other Pb fractions and all Zn and Cd fractions were significantly related ($p < 0.05$) to industrial land-use (I) proportion. These results suggest that industrial land use may be an important

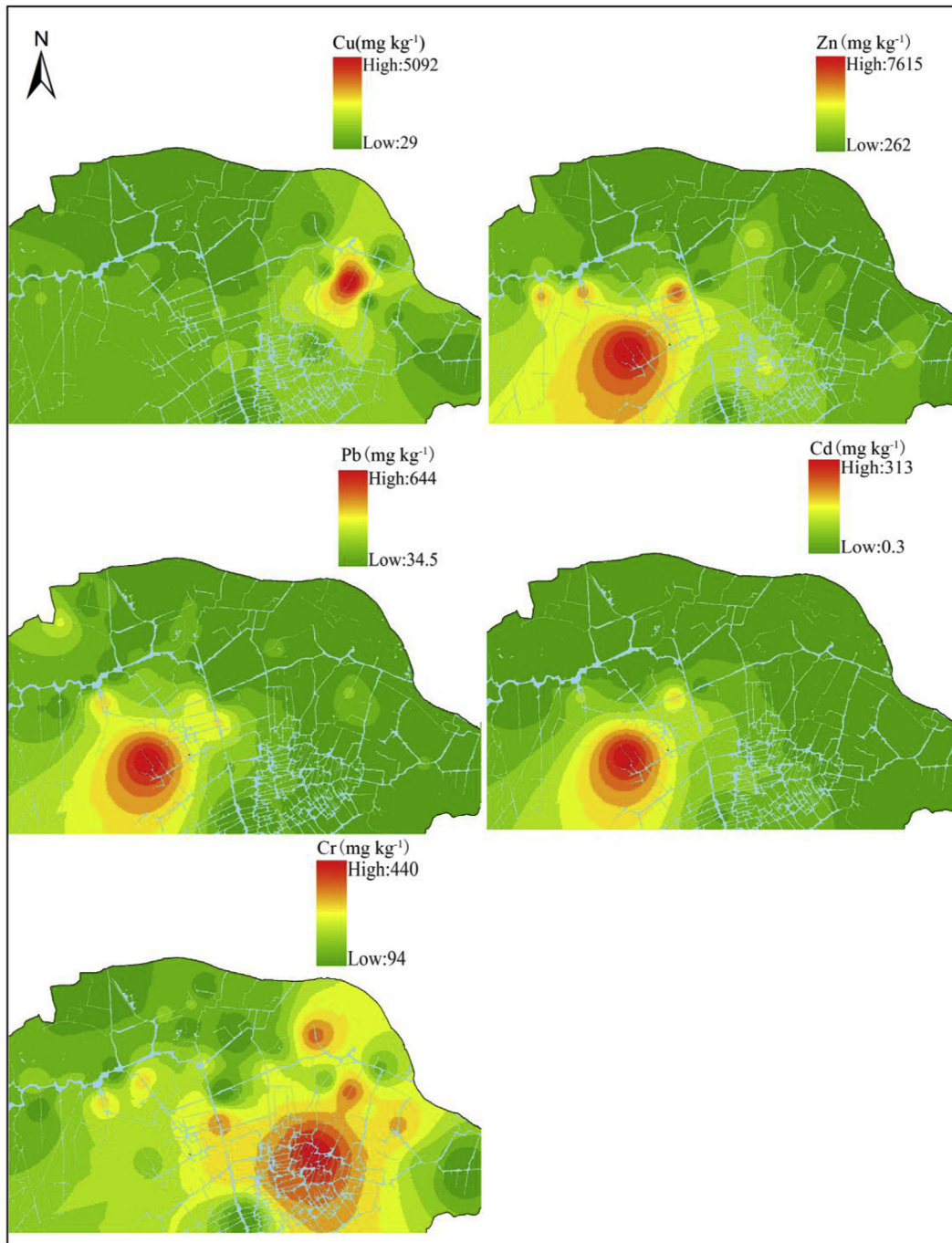


Fig. 2. Total heavy metal concentrations in Wen-Rui Tang River sediments.

factor influencing the concentrations of various Zn, Pb and Cd fractions. Land-use relationships for Cu varied among Cu fractions. The concentration of Exch-Cu was partially explained by the combination of agricultural (A), industrial (I), and ecological (E) land uses. The Exch-Cu fraction was related to industrial land use while Red-Cu and Res-Cu fractions showed no significant link to land use. In contrast, neither stepwise regression nor GWR indicated strong relationships between various Cr fractions and land use. This lack of relationship for Cr is consistent with the PCA results that suggested Cr pollution may be derived from a different source than the other metals.

Based on the general GWR results, several metal fractions with

high R^2 values were further analyzed to explore their local variation. Industrial land proportion had an appreciable influence on the spatial variation of various Zn, Pb and Cd fractions in sediments. Generally, most sampling sites had local positive relationships between industrial land proportion and heavy metal fractions. In contrast, a few sites in the eastern portion of the watershed displayed local negative relationships with industrial land proportion. The dissimilarity of local R^2 values among all sampling sites indicated that spatial heterogeneity of metal fractions in sediments was influenced by industrial land-use proportion. In general, sites with high industrial land use were accompanied by high local R^2 values. Org-Cu was the only Cu fraction to show a significant correlation

Table 2
Principle component rotation matrix of heavy metals.

	PC1	PC2	PC3
Explained variance (%)	47.9	14.2	13.8
Cumulative variance (%)	47.9	62.1	75.9
Exch-Cu	-0.109	0.941	0.262
Red-Cu	0.062	0.054	0.194
Org-Cu	0.057	0.966	0.152
Res-Cu	0.240	0.892	0.204
Exch-Zn	0.846	0.054	0.094
Red-Zn	0.943	0.033	0.075
Org-Zn	0.903	0.083	0.069
Res-Zn	0.900	0.089	0.062
Exch-Pb	0.940	0.028	-0.114
Red-Pb	0.957	0.088	-0.077
Org-Pb	0.835	0.138	0.289
Res-Pb	0.497	-0.041	0.052
Exch-Cd	0.950	-0.018	0.123
Red-Cd	0.964	0.000	-0.035
Org-Cd	0.981	-0.016	0.021
Res-Cd	0.837	-0.055	0.224
Exch-Cr	0.102	0.347	0.861
Red-Cr	-0.015	0.128	0.911
Org-Cr	0.125	0.171	0.902
Res-Cr	0.083	0.039	0.087

Bold values represent the high loadings in this principle.

Table 3
Comparison of stepwise regression and GWR models.

	Stepwise regression model	Regression R ²	GWR R ²
Exch-Cu	0.78 (A) + 0.64(I) + 0.012(E)	0.266	0.283
Red-Cu	0.14 (A) - 0.65 (E)	0.016	0.025
Org-Cu	14.7 (I) - 10.9	0.137	0.404
Res-Cu	1.2 (I) + 27.2	0.094	0.117
Exch-Zn	13.7 (I) + 474.3	0.121	0.558
Red-Zn	16.4 (I) + 153.9	0.161	0.660
Org-Zn	8.4 (I) + 140.0	0.166	0.554
Res-Zn	1.6 (I) + 70.5	0.187	0.612
Exch-Pb	0.75 (I) - 3.4	0.229	0.892
Red-Pb	2.1 (I) + 5.0	0.261	0.865
Org-Pb	1.2 (I) + 18.5	0.197	0.582
Res-Pb	1.0 (I) + 36.3	0.087	0.223
Exch-Cd	0.93 (I) - 1.5	0.169	0.762
Red-Cd	0.89 (I) - 0.47	0.204	0.807
Org-Cd	0.23 (I) - 1.1	0.225	0.863
Res-Cd	0.13 (I) + 0.28	0.130	0.577
Exch-Cr	-0.025 (U) + 0.022 (I) + 4.0	0.202	0.258
Red-Cr	-0.064 (U) + 0.006 (I) + 8.6	0.188	0.247
Org-Cr	-1.1 (U) + 140.6	0.076	0.047
Res-Cr	0.64 (I) + 108.8	0.028	0.056

I=Industrial land; U= Urban land; A = Agriculture land; E = Ecological land. In GWR model, the single variable model used R² and multivariate model used adjusted R². Bold values in regression represent significance at the 0.05 level.

with industrial land-use proportion, resulting in a distinct spatial distribution pattern compared with the other Cu fractions. High coefficients, as well as high local R² values, were identified in the eastern industrial region, while lower coefficients were found in the western portion of the watershed (Fig. S3). A similar distribution pattern for local R² values was found for all Zn, Pb and Cd fractions; however, the western sites had higher local R² values. Additionally, local R² values in the southwestern sites, which were mainly located in the old industrial region, were higher than those for the northeastern sites.

Local spatial variation was also found among various fractions of the same metal. The local R² values for Zn in the northern sites were identified as having a decreasing trend from the exchangeable fraction to residual fraction (Fig. 3). The local R² values for Exch-Pb in the southern sampling sites of the watershed were greater than

those for Red-Pb and Org-Pb, demonstrating that industrial lands more strongly affected Exch-Pb (Fig. S4). In contrast, Org-Pb was identified with greater local R² values for sites in the northwestern portion of the watershed, while Exch-Pb showed smaller R² values. The spatial variation of local R² values among different metal fractions was more complex with respect to Cd (Fig. 4). Exch-Cd and Res-Cd showed greater R² values than Red-Cd and Org-Cd in the northwestern region, while Res-Cd in the southern watershed had lower R² values compared to Exch-Cd, Red-Cd and Org-Cd.

4. Discussion

4.1. Heavy metal pollution of riverine sediments

Compared with local background metal concentrations, metal concentrations in other watersheds, and heavy metal sediment guidelines, Wen-Rui Tang River sediments exhibit appreciably elevated metal levels (Table 1). Using the CV as a measure of spatial variability (low = CV < 10% and high = CV > 90%) indicates high spatial variability for Cu, Zn, Pb and Cd. These results imply anthropogenic input of metals into the sediment environment as background concentrations of elements are relative stable within a local region and should thereby have low CVs (Manta et al., 2002). The high concentrations and CVs for Cu, Zn, Pb and Cd may be ascribed to emissions of industrial wastes and wastewater into the aquatic environment. In particular, electroplating, printing and dyeing, paper mills, tanning, chemical and synthetic leather are primary industries located within the study area. These factories have historically discharged non-treated industrial effluents with high concentrations of heavy metals into Wen-Rui Tang River and are considered an important metal pollution source (Srinivasa et al., 2010). In addition, the significant positive correlation of metals with OM indicates that sediment characteristics also play an important role in heavy metal concentrations and fractionation (Yu et al., 2001). In contrast, Cr had a relative low CV value compared to the other metals, which may demonstrate a different pollution source (discussed in next section).

4.2. Distribution and source analysis of heavy metal speciation

Interpolation methods provide a powerful approach to explore spatial patterns of pollutants for source determination. Spatial distributions for Zn, Pb and Cd showed a similar pattern with a 'hot spot' in the southwestern portion of the watershed, which was the location of the older industrial zone (Fig. 2). Strong correlations among Zn, Pb and Cd concentrations further support a common pollution source for these metals, while Cr was only correlated with Cu. With the exception of Cr, the strong positive correlation among heavy metals was similar with an investigation of a river-reservoir system in the Democratic Republic of Congo (Mwanamoki et al., 2014). The PCA analysis provides additional support for a common source of Zn, Pb and Cd as several species of these heavy metals demonstrated a significant loading weight on PC1. Previous studies indicated that these metals could have a common source and similar transport pathways in urban rivers (Kilunga et al., 2017). Although significantly correlated with the other metals, Cu showed a different spatial pattern and high loading on PC2, which suggests a contrasting pollution source. A 'hot spot' for Cu was also identified in the eastern portion of the study area, which was the location of a newer industrial zone. Elevated Exch-Cu (21.3%) and Total-Cu (387.6 mg kg⁻¹) concentrations at site B23 in the western watershed were anomalously higher compared to adjacent sampling sites. Agriculture lands surrounding B23 accounted for 46.1% of total land use. Previous research has demonstrated that agricultural activities may contribute Cu pollution to the environment,

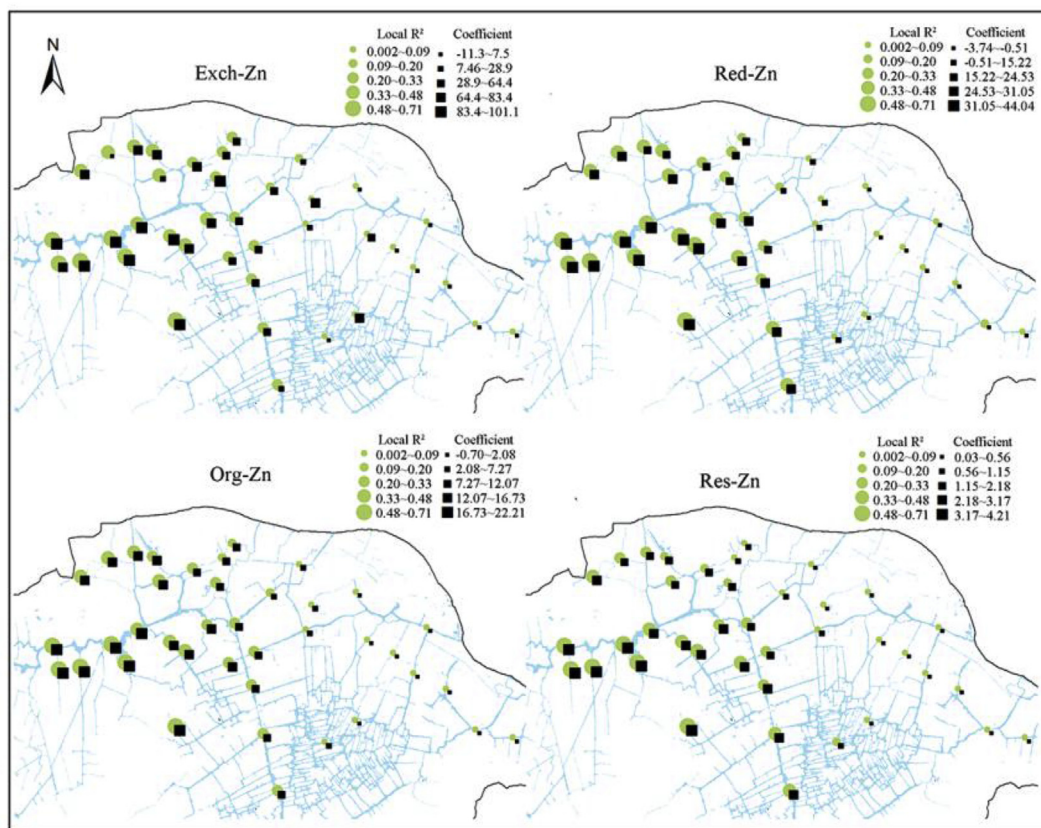


Fig. 3. Relationship between different Zn fractions and industrial land.

such as from fertilizer and pesticide applications (Marrugo-Negrete et al., 2017; Li et al., 2013). In addition, the regression model showed correlation with several land-use types, indicating that Cu in the sediment likely originated from multiple sources in this area.

A significant contribution of the residual Cr fraction (62.4%) was identified in the study area, which was ascribed to its low mobility in the absence of strongly oxidizing or reducing conditions (Kabata-Pendias and Pendias, 1992). Chromium in sediments displayed a decreasing trend from east to west, with a distinct 'hot spot' in the southeastern portion of the study area that was not observed for the other metals (Fig. 2). The sites with relatively higher Cr concentrations were mainly located in the industrial regions. Higher organically bound Cr was generally found in areas with higher total Cr concentrations. Based on correlation and PCA analyses, Cr only showed a relationship with Cu and was the only metal to show a high loading weight on PC3. The tanning industry, which was a historically abundant industry in the study area, is a known source of Cr contamination (Srinivasa et al., 2010); however, the Cr contamination levels in our study area were low compared to the other metals. Song et al. (2012) reported Cr contents of 43.9–1892.7 mg kg⁻¹ in sediments in Wen-Rui Tang River, which were similar or higher than the Cr concentrations found in this study (94.2–439.6 mg kg⁻¹). Recent regulatory actions in the Wen-Rui Tang River watershed have reduced Cr in effluents by 2706.9 kg yr⁻¹ via an emissions reduction strategy since 2013 (WEPB, 2014). The recent reduction in Cr discharge to rivers is consistent with the unique nature of Cr among the metals for loading on PC3 and may be attributed to the recent Cr pollution control strategies that have resulted in lower Cr concentrations in recent riverine sediments.

4.3. Relationship between land-use types and heavy metal pollution based on GWR

Land-use types as classified by human activities are often reasonable indicators of potential metal contamination in the environment (Li et al., 2017a, b). The stepwise regression model combined with manual selection of land-use types effectively improved the R² value of the GWR models, which was consistent with Tu (2013). The various Cu fractions were correlated with multiple land-use types, including agricultural, industrial and ecological lands (Table 3). We interpret this finding to indicate a mixture of Cu pollution sources contributing to Cu contamination of the sediments. The non-significant regression correlations for all Cu species, except organically-bound Cu, reflect the strong complexation of Cu by organic materials in the sediment. In contrast to Cu, all Zn, Pb and Cd fractions (except Res-Pb) had strong correlations with industrial land proportion. We ascribe these significant correlations to reflect the dominance of industrial activities as the primary source of these metals in the watershed sediments. Anthropogenic industrial emissions of metal pollutants include atmospheric deposition (e.g., waste gas), effluent and solid residue releases containing heavy metals (Gao et al., 2015; De et al., 2016). Consistent with PCA, the non-significant regression correlations for Cr fractions with land use suggest that the source of Cr is distinctly different from Zn, Pb and Cd.

The GWR model considers the spatial heterogeneity of pollutant distribution and the distribution of local R² values (Fig 3–4, S3–S4). Higher local R² values (0.32–0.39) for Org-Cu in the eastern industrial zone stem from the dominance of Cu inputs from industrial activities and its preferential incorporation into organic complexes. The absence of a significant correlation for local R² values of Org-Cu

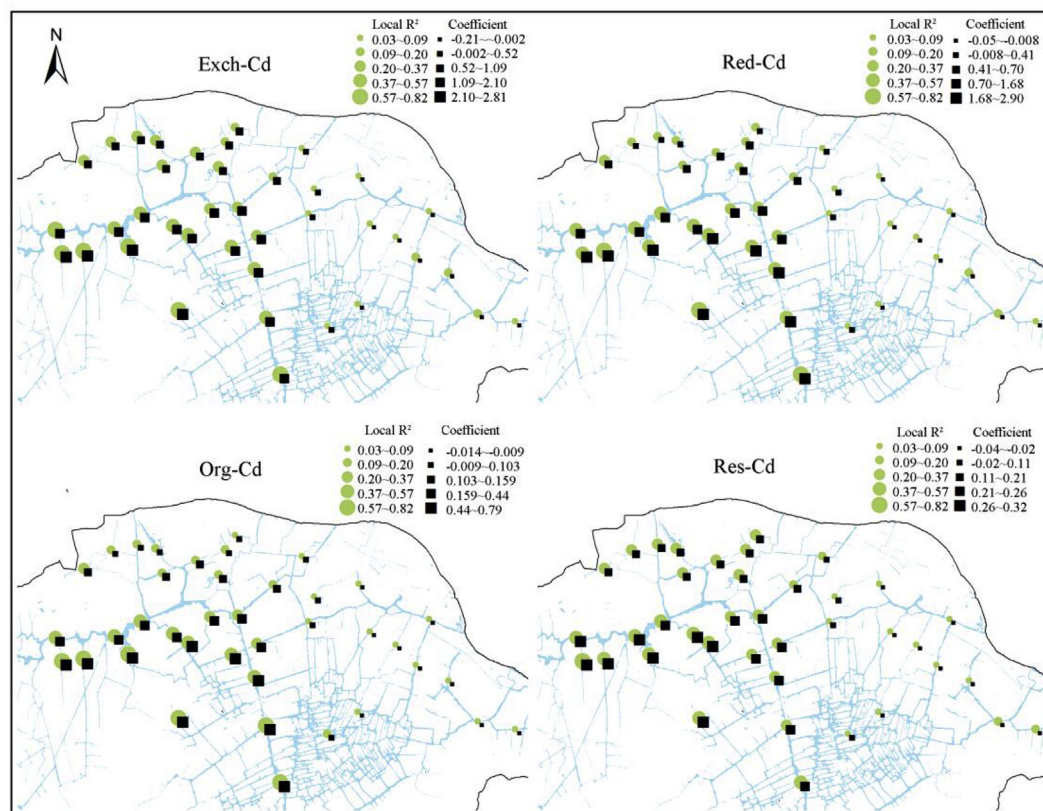


Fig. 4. Relationship between different Cd fractions and industrial land.

with other heavy metal fractions suggest a different industrial pollution source for Cu compared to the other metals in this watershed (except for Res-Pb). The similar distribution patterns for local R^2 values among the various Zn, Pb and Cd fractions, combined with their significant correlation with industrial land proportion, demonstrate that these heavy metals are likely associated with similar industrial activities. For example, Samaniego et al. (2007) reported a common source for Zn, Pb and Cd pollution from spent pickling effluents, which was also a major industry within our study area. The decreasing trend of local R^2 values for Zn, Pb and Cd from southwest to the north was consistent with a decreasing proportion of industrial activity, indicating a diminishing impact from industrial land use on metal pollution of riverine sediments. However, significant correlations for local R^2 values and industrial land-use proportion were not found at the watershed scale, indicating other factors (e.g., sediment characteristics, contrasting metal pollution sources, changing land-use type during rapid urbanization, etc.) contributing to metal fraction distribution at the watershed scale (Zhang et al., 2014).

Various Zn and Pb fractions showed similar local R^2 values in the southwestern region, demonstrating the influence of industrial activities on metal contamination in this intensive industrial zone. However, the local R^2 values for the contrasting metal fractions varied within the watershed. Decreasing local R^2 values of Exch-Zn relative to Res-Zn in the northern portion of the watershed indicate that the most mobile Zn fractions were most strongly correlated with industrial pollution. In contrast, the more stable Zn fractions were more likely impacted by background metal sources and sediment characteristics, such as redox, pH and organic matter (Guo et al., 1997; Gao et al., 2015). Local R^2 values for Pb fractions followed: Org-Pb > Red-Pb > Exch-Pb. This may reflect chemical

transformations of Pb within the sediment environment resulting in preferential complexation of Pb with organic matter as the most stable form (Strawn and Sparks, 2000). The spatial distribution pattern for local R^2 values for various Cd fractions was generally constant throughout the study area. This may indicate the importance of the industrial pollution source rather than the sediment environment in controlling concentrations and chemical fractionation. Cadmium is not a redox sensitive species and forms weak organic complexes relative to Cu and Pb, thereby limiting its interactions with the sediment and leading to a weaker correlation than for the other metals. Sites with high local R^2 values (>0.3) for the various Cd fractions generally had a higher relative proportion of industrial lands and were mainly located in the older industrial zone. The strength of this positive relationship weakened in less industrialized areas in the eastern portion of the study area reflecting the importance of industrial activities on Cd distribution.

5. Conclusions

This study investigated the distribution of heavy metal contaminants in sediments of the Wen-Rui Tang River watershed, an area that has experienced rapid urbanization and industrialization over the past several decades. Multivariate statistical analyses, as well as GIS technology, were applied to identify the spatial heterogeneity of metals in sediments (and metal fractions) with respect to land-use type. This investigation consisted of four components: (1) total and various chemical fractions of Cu, Zn, Pb, Cd and Cr in riverine sediments, (2) corresponding spatial variation, (3) identification of metal pollution sources, and (4) exploration of general and local relationships between different land-use types and different metals and their corresponding chemical fractions.

The major results of this study were as follows:

- (1) Wen-Rui Tang River sediments suffer from severe heavy metal contamination, especially for Cd pollution, which exceeded the local background value for all sampling sites and had an average concentration 100 times higher than local background levels. Copper and Zn concentrations were approximate 10 times higher than local background values, followed by Cr at nearly 2 times higher. In terms of chemical fractions, the exchangeable fraction was dominant for Zn and Cd, which pose high bioavailability and potential toxicity risk, while Pb, Cr and Cu were mainly found in the residual and organic bound fractions; organically bound Cu comprised a large portion of the total Cu concentration. Therefore, the sediment environment, such as OM, likely plays an important role in heavy metal fractionation in the study region.
- (2) The highest concentrations of heavy metals were detected in the industrial regions with high spatial variation among metals. The location of the older, traditional industrial zone was identified as a 'hot spot' for Zn, Pb and Cd. The highest Cu concentrations were in the eastern region, while Cr showed a relatively uniform distribution within the study area. In addition, spatial patterns varied for different metal fractions, and the dominant metal fractions differed from total concentration distribution patterns across the watershed.
- (3) Regression analysis was consistent with PCA results, which identified a similar industrial pollution source for Zn, Pb and Cd, and suggested a combination of industrial and agricultural sources for Cu. The absence of a significant correlation for Cr with the other metals was confirmed by its unique high loading on PC3. It is possible that Cd distribution has been influenced by effective Cd pollution control strategies implemented by the local government in the past decade.
- (4) Both regression and GWR models indicated a significant and positive correlation between industrial land-use proportion and various Zn, Pb and Cd fractions. Org-Cu was significantly correlated with industrial land use, while no significant relationship was found between Cr fractions and land-use type. Local R^2 values from GWR indicated that spatial variation of heavy metals was due to different proportions of industrial land use.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.05.090>.

References

Adams, S.V., Quraishi, S.M., Shafer, M.M., Passarelli, M.N., Freney, E.P., Chlebowski, R.T., Luo, J., Meliker, J.R., Mu, L., Neuhauser, M.L., 2014. Dietary cadmium exposure and risk of breast, endometrial, and ovarian cancer in the Women's Health Initiative. *Environ. Health Perspect.* 122, 594–600.

Bhowmik, A.K., Alamdar, A., Katsoyiannis, I., Shen, H., Ali, N., Ali, S.M., Bokhari, H., Schäfer, R.B., Eqani, S.A., 2015. Mapping human health risks from exposure to trace metal contamination of drinking water sources in Pakistan. *Sci. Total Environ.* 538, 306–316.

Bielicka-Gleidoń, A., Rytko, E., Żamojć, K., 2013. Distribution, bioavailability and fractionation of metallic elements in allotment garden soils using the BCR

sequential extraction procedure. *Pol. J. Environ. Stud.* 22, 1013–1021.

Chen, H., Arocena, J.M., Li, J., Thring, R.W., Zhou, J., 2012. Mobility and storage sinks for chromium and other metals in soils impacted by leather tannery wastes. *J. Environ. Monit.* 14, 3240–3248.

Chen, Q., Mei, K., Dahlgren, R.A., Wang, T., Jian, G., Zhang, M., 2016. Impacts of land use and population density on seasonal surface water quality using a modified geographically weighted regression. *Sci. Total Environ.* 572, 450–466.

Chowdhury, S., Mazumder, M.A., Alattas, O., Husain, T., 2016. Heavy metals in drinking water: occurrences, implications, and future needs in developing countries. *Sci. Total Environ.* 569–570, 476–488.

De, M.G.P., Navoni, J.A., De, M.F.D., Do Amaral, V.S., 2016. Ecotoxicological water assessment of an estuarine river from the Brazilian Northeast, potentially affected by industrial wastewater discharge. *Sci. Total Environ.* 572, 324–332.

Ebrahimpour, M., Mushrifah, I., 2008. Heavy metal concentration in water and sediments in Tasik Chini, a freshwater lake, Malaysia. *Environ. Monit. Assess.* 141, 297–307.

Fotheringham, A.S., Brunsdon, C., Charlton, M., 2002. *Geographically Weighted Regression: the Analysis of Spatially Varying Relationships*. Wiley, Chichester, UK.

Gao, X., Gu, Y., Xie, T., Zhen, G., Huang, S., Zhao, Y., 2015. Characterization and environmental risk assessment of heavy metals in construction and demolition wastes from five sources (chemical, metallurgical and light industries, and residential and recycled aggregates). *Environ. Sci. Pollut. Res.* 22, 9332–9344.

Goretti, E., Pallottini, M., Ricciarini, M.I., Selvaggi, R., Cappelletti, D., 2016. Heavy metals bioaccumulation in selected tissues of red swamp crayfish: an easy tool for monitoring environmental contamination levels. *Sci. Total Environ.* 559, 339–346.

Guo, T., DeLaune, R.D., Patrick, W.H., 1997. The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment. *Environ. Int.* 23, 305–316.

Kabata-Pendias, A., Pendias, H., 1992. *Trace Elements in Soil and Plants*. CRC Press Inc, Boca Raton, Florida.

Ke, X., Gui, S.F., Huang, H., Zhang, H.J., Wang, C.Y., Guo, W., 2017. Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. *Chemosphere* 175, 473–481.

Kilunga, P.I., Sivalingam, P., Laffite, A., Grandjean, D., Mulaji, C.K., de Alencastro, L.F., Mpiana, P.T., Poté, J., 2017. Accumulation of toxic metals and organic micro-pollutants in sediments from tropical urban rivers, Kinshasa, Democratic Republic of the Congo. *Chemosphere* 179, 37–48.

Lanphear, B.P., Hornung, R., Khoury, J., Yolton, K., Baghurst, P., Bellinger, D.C., Canfield, R.L., Dietrich, K.N., Bornschein, R., Greene, T., 2005. Low-level environmental lead exposure and children's intellectual function: an international pooled analysis. *Environ. Health Perspect.* 113, 894–899.

Li, F., Huang, J., Zeng, G., Yuan, X., Li, X., Liang, J., Wang, X., Tang, X., Bai, B., 2013. Spatial risk assessment and sources identification of heavy metals in surface sediments from Dongting Lake, Middle China. *J. Geochem. Explor.* 132, 75–83.

Li, X., Shi, X., Wang, A., Li, Y., 2017a. Heavy metals contamination and assessment in gas station dust of Xi'an, a mega-city of China. *Environ. Earth. Sci.* 76, 288.

Li, Y., Arocena, J.M., Qiao, Z., Thring, R.W., Li, J., 2017b. Heavy metals and nutrients (carbon, nitrogen, and phosphorus) in sediments: relationships to land uses, environmental risks, and management. *Environ. Sci. Pollut. Res.* 24, 7403–7412.

Liu, J., Duan, C.Q., Zhu, Y.N., Zhang, X.H., Wang, C.X., 2007. Effect of chemical fertilizers on the fractionation of Cu, Cr and Ni in contaminated soil. *Environ. Geol.* 52, 1601–1606.

Lu, R.K., 2000. *Chemical Analysis Method of Agricultural Soil China*. Agricultural Technology Press, Beijing (2000) (in Chinese).

Manta, D.S., Angelone, M., Bellanca, A., Neri, R., Sprovieri, M., 2002. Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Sci. Total Environ.* 300, 229–243.

Marrugo-Negrete, J., Pinedo-Hernández, J., Díez, S., 2017. Assessment of heavy metal pollution, spatial distribution and origin in agricultural soils along the Sinú River Basin, Colombia. *Environ. Res.* 154, 380–388.

McMillen, D.P., 2004. Geographically weighted regression: the analysis of spatially varying relationships. *Am. J. Agric. Econ.* 86, 554–556.

Müller, G., 1979. Schwermetalle in den Sedimenten des Rheins—veränderungen seit 1971. *Umschau* 24, 773–778.

Mwanamoki, P.M., Devarajan, N., Thevenon, F., Niane, B., de Alencastro, L.F., Grandjean, D., Mpiana, P.T., Prabakar, K., Mubedi, J.L., Kabele, C.G., Wildi, W., Poté, J., 2014. Trace metals and persistent organic pollutants in sediments from river-reservoir systems in Democratic Republic of Congo (DRC): spatial distribution and potential ecotoxicological effects. *Chemosphere* 111, 485–492.

Pan, K., Wang, W.X., 2012. Trace metal contamination in estuarine and coastal environments in China. *Sci. Total Environ.* 421–422, 3–16.

Pourreza, N., Ghanemi, K., 2009. Determination of mercury in water and fish samples by cold vapor atomic absorption spectrometry after solid phase extraction on agar modified with 2-mercaptobenzimidazole. *J. Hazard Mater.* 161, 982–987.

Pueyo, M., Mateu, J., Rigol, A., Vidal, M., López-Sánchez, J.F., Rauret, G., 2008. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environ. Pollut.* 152, 330–341.

Qiao, Y., Yang, Y., Gu, J., Zhao, J., 2013. Distribution and geochemical speciation of heavy metals in sediments from coastal area suffered rapid urbanization, a case study of Shantou Bay, China. *Mar. Pollut. Bull.* 68, 140–146.

Quevaullier, P., Rauret, G., López-Sánchez, J.F., Rubio, R., Ure, A., Muntau, H., 1997. Certification of trace metal extractable contents in a sediment reference

- material (CRM 601) following a three-step sequential extraction procedure. *Sci. Total Environ.* 205, 223–234.
- Rosado, D., Usero, J., Morillo, J., 2016. Ability of 3 extraction methods (BCR, Tessier and protease K) to estimate bioavailable metals in sediments from Huelva estuary (Southwestern Spain). *Mar. Pollut. Bull.* 102, 65–71.
- Sakan, S., Popović, A., Škrivanj, S., Sakan, N., Đorđević, D., 2016. Comparison of single extraction procedures and the application of an index for the assessment of heavy metal bioavailability in river sediments. *Environ. Sci. Pollut. Res.* 23, 1–16.
- Samaniego, H., Román, M.F.S., Ortiz, I., 2007. Kinetics of zinc recovery from spent pickling effluents. *Ind. Eng. Chem. Res.* 46, 907–912.
- Sarkar, B., 2009. *Heavy Metals in the Environment*. CRC Express Inc, Boca Raton, Florida.
- Simpson, S.L., Ward, D., Strom, D., Jolley, D.F., 2012. Oxidation of acid-volatile sulfide in surface sediments increases the release and toxicity of copper to the benthic amphipod *Melita plumulosa*. *Chemosphere* 88, 953–961.
- Smith, S.L., MacDonald, D.D., Keenleyside, K.A., Ingersoll, C.G., Field, J., 1996. A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *J. Great Lake. Res.* 22, 624–638.
- Song, L., Gu, D.G., Huang, M.S., Chen, L., Huang, Q.C., He, Y., 2012. Spatial distribution and contamination assessments of heavy metals in sediments of Wenzhou River Network (in Chinese). *Spectrosc. Spectr. Anal.* 32, 2540–2545.
- Srinivasa, G.S., Ramakrishna, R.M., Govil, P.K., 2010. Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. *J. Hazard Mater.* 174, 113–121.
- Strawn, D.G., Sparks, D.L., 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. *Soil Sci. Soc. Am. J.* 64, 144–156.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844–851.
- Tu, J., 2013. Spatial variations in the relationships between land use and water quality across an urbanization gradient in the watersheds of Northern Georgia, USA. *Environ. Manag.* 51, 1–17.
- Tu, J., Xia, Z.G., 2008. Examining spatially varying relationships between land use and water quality using geographically weighted regression I: model design and evaluation. *Sci. Total Environ.* 407, 358–378.
- Wang, L., Meng, J., Li, Z.T., Liu, X.M., Xia, F., Xu, J.M., 2017. First “charosphere” view towards the transport and transformation of Cd with addition of manure derived biochar. *Environ. Pollut.* 227, 175–182.
- Wang, Q.H., Dong, Y.X., Zheng, W., Zhou, G.H., 2007. Soil geochemical baseline values and environmental background values in Zhejiang, China (in Chinese). *Geol. Bull. China* 26, 590–597.
- Wang, X.Y., Zhou, Y., Yang, H.S., Wang, Q., Liu, S.L., 2010. Investigation of heavy metals in sediments and Manila clams *Ruditapes philippinarum* from Jiaozhou Bay, China. *Environ. Monit. Assess.* 170, 631–643.
- Wenzhou Environmental Protection Bureau (WEPB), 2014. Wenzhou Environment Quality Report for 2013 (In Chinese). Wenzhou, China.
- Williams, M., Hopkinson, C., Rastetter, E., Vallino, J., Claessens, L., 2005. Relationships of land use and stream solute concentrations in the Ipswich River basin, Northeastern Massachusetts. *Water, Air, Soil Pollut.* 161, 55–74.
- Wong, K.W., Yap, C.K., Nulit, R., Hamzah, M.S., Chen, S.K., Cheng, W.H., Karami, A., Alshami, S.A., 2017. Effects of anthropogenic activities on the heavy metal levels in the clams and sediments in a tropical river. *Environ. Sci. Pollut. Res.* 24, 116–134.
- Wright, D.A., Welbourn, P., 2002. *Environmental Toxicology*. Cambridge University Press, Cambridge, U.K.
- Wu, S.S., Yang, H., Guo, F., Han, R.M., 2016. Spatial patterns and origins of heavy metals in Sheyang River catchment in Jiangsu, China based on geographically weighted regression. *Sci. Total Environ.* 580, 1518–1529.
- Yu, K.C., Tsai, L.J., Chen, S.H., Ho, S.T., 2001. Correlation analyses on binding behavior of heavy metals with sediment matrices. *Water Res.* 35, 2417–2428.
- Zhang, C., Yu, Z.G., Zeng, G.M., Jiang, M., Yang, Z.Z., Cui, F., Zhu, M.Y., Shen, L.Q., Hu, L., 2014. Effects of sediment geochemical properties on heavy metal bioavailability. *Environ. Int.* 73, 270–281.