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Assessment of the Geographical Detector Method for investigating heavy metal source apportionment in an urban watershed of Eastern China



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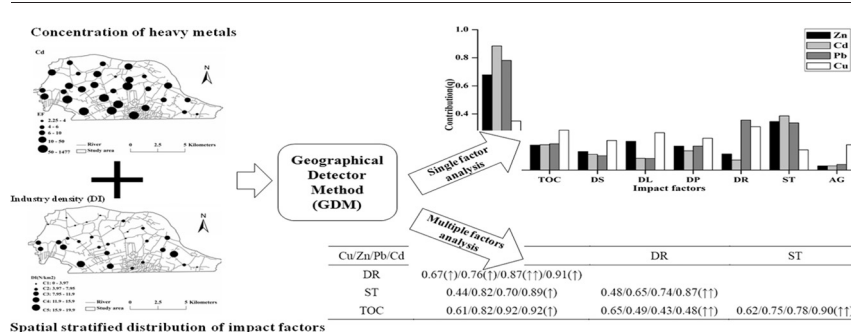
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HIGHLIGHTS

- Geographical Detector Method identifies key factors contributing to metal pollution.
- GDM guides riverine sediment metal source apportionment and remediation.
- GDM uses spatial variance to assess metal influencing factors at watershed scale.
- GDM assesses additive and nonlinear interactions among human and natural factors.

GRAPHICAL ABSTRACT



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ABSTRACT

Assessing heavy metal pollution in river sediments and identifying the key factors contributing to metal pollution are critical components for devising river environmental protection and remediation strategies to protect human and ecological health. This is especially important in urban areas where metals from a wide range of sources contribute to sediment pollution. In this study, the metal enrichment factor (EF) was used to measure the watershed distribution of Cu, Zn, Pb and Cd in sediments in the Wen-Rui Tang urban river system in Wenzhou, Eastern China. The Geographical Detector Method (GDM) was specifically evaluated for its ability to analyze spatial relationships between metal EFs and their anthropogenic and natural control factors, including densities of industry (DI), livestock (DL), service industries (DS), population (DP), and roads (DR), along with agricultural area (AG), sediment total organic carbon (TOC), and soil types (ST). Results showed that the watershed was highly contaminated by all metals with an EF trend of Cd >> Zn > Cu > Pb. The spatial distribution of EFs demonstrated high contamination of all metals in the southwestern region of the watershed where industrial activities were concentrated, and higher Cu and Zn concentrations in the northeastern region having a high density of livestock production. GDM results identified DI as the dominant determinant for all metals, while TOC and ST were determined to have a moderate secondary influence for Zn, Pb and Cd. Additionally, GDM revealed several additive and nonlinear interactions between anthropogenic and natural factors influencing metal concentrations. Compared to other correlation, multiple linear regression and geographically weighted regression, GDM demonstrated distinct advantages of being able to assess both categorical and continuous variables and determine both single and multiple factor interactions. These attributes provide a more comprehensive understanding of metal spatial

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distributions while avoiding multicollinearity issues when identifying significant contributing factors at the watershed scale.

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1. Introduction

River sediments are an essential component of the aquatic environment having a strong control in buffering metals concentrations in the aqueous phase and regulating metal bioavailability to benthic organisms (Stead-Dexter and Ward, 2004). Metal pollution in aquatic ecosystems has captured global attention due to their ability to bioaccumulate/biomagnify in the food web (Ke et al., 2017; Li et al., 2016). This may result in serious toxicity, including to humans using aquatic organisms as a food source or using the contaminated waters as a source of drinking water or irrigation for food crops (Stankovic et al., 2014; Baby et al., 2010). Both anthropogenic activities, such as industrial and domestic wastewater inputs, and natural weathering of rocks contribute to metal contamination of sediments (Akçay et al., 2003). Anthropogenic activities are generally the cause of most metal pollutants and these metal sources often have a higher bioaccessibility resulting in more severe toxicity impacts on aquatic ecosystems (Sekabira et al., 2011). However, given the background level of metals coming from natural processes, it is very important to develop techniques to help separate anthropogenic versus natural (i.e., background) contributions for effective mitigation and management.

In recent years, considerable research has examined anthropogenic influences to metal pollution in river sediments by integrating multiple indicators (e.g., ecological risk assessment, enrichment factor, and geoaccumulation index) (Zhang et al., 2017; Islam et al., 2015; Sekabira et al., 2010). Statistical methods examining the sources of metal pollution include Pearson correlation coefficient analysis (Bastami et al., 2015), stepwise multiple regression analysis (Wu et al., 2017), principle component analysis (Bai et al., 2016) and geographically weighted regression (GWR) (Xia et al., 2018). Although these methods can often measure and estimate metal enrichment in sediments with various influencing factors, they neglect the spatial relationship between the driving factors and metal concentrations or are hindered by multicollinearities among the influencing factors (Comber et al., 2018; Wheeler and Tiefelsdorf, 2005). To overcome these limitations, the Geographical Detector Method (GDM) was applied in this study to use the spatial variance to test and investigate the relative contribution of a single factor and the interactions between independent variables, thus providing an objective measure of spatially stratified heterogeneity (Wang et al., 2016). GDM was first applied to study neural tube defects in the Heshun Region, China (Wang et al., 2010). Subsequently, GDM was used to examine the influence of environmental factors on vegetation in temperate, arid regions (Ren et al., 2014), to examine the relevant factors influencing rural settlement distribution at the county level (Yang et al., 2016), and to analyze the factors influencing soil metal transport and deposition in rainfall from Huanjiang County, South China (Qiao et al., 2017). From these studies, it was recognized that GDM could be effectively used to study the relationships between environmental factors and metal pollution. Therefore, we applied the GDM to examine the relationships between metals and anthropogenic/natural factors in riverine sediments in a complex watershed ranging from rural to highly urbanized/industrialized regions. The GDM approach was compared to other analysis methods to provide validation for the analysis and to assess the advantages/disadvantages of the GDM to other approaches.

Wenzhou, a city of 9.2 million population, was the birthplace of entrepreneur activities in China that led to the establishment of many small- and medium-sized commercial enterprises. Leather products, machinery and hardware manufacturing, electroplating, printing and

dyeing, and chemical products are some of the dominant enterprises contributing metal emissions to the environment. Much of the municipal and industrial waste waters were historically discharged directly to receiving waters with no treatment (WEPPB, 2014). While much of the wastewater in Wenzhou is currently collected, there are still large inputs of metals to city waterways as the treatment methods are ineffective at metal removal (Gobeil et al., 2005). Previous research in the Wen-Rui Tang River watershed focused on identifying the spatial distribution and sources of water pollutants (Yang et al., 2013), the spatial distribution and seasonal variation of methylmercury (Pan et al., 2017), and risk assessment of heavy metal pollution on human health (Qu et al., 2018). However, these studies did not analyze the contributions of various influencing factors to metal concentrations in riverine sediments. Investigating source apportionment is important for effective identification of metals pollution sources (Singh and Kuman, 2017).

Therefore, the primary objective of this study was to integrate enrichment factor characterization of metal contamination with GDM to (1) assess the pollution level of metals in riverine surface sediments and identify the spatial distribution of metals pollution in the watershed; (2) analyze the contribution of anthropogenic activities and natural factors affecting metal concentrations; (3) explore synergistic and/or antagonistic interactions among anthropogenic activity factors and natural factors; and (4) compare the advantages/disadvantages of GDM to other statistical methods. Development of the GDM for spatial assessment of environmental pollutants at the watershed scale provides an important tool for environmental and water resource agencies to develop sustainable environmental management and remediation strategies.

2. Material and methods

2.1. Study area

The Wen-Rui Tang River watershed (740 km²) is located in Wenzhou, Zhejiang Province, in the Eastern China (Fig. 1). Land use ranges from rural to urban and the watershed has experienced rapid urbanization in the past decades. According to the 2015 Wenzhou Environmental Status Bulletin, there are a total of 1151 companies comprising six major industrial categories of electroplating, printing and dyeing, papermaking, leather processing, chemical production, and synthetic leather. Annual sewage discharge in the watershed is ~20 million tons with ~40% of the sewage load being discharged directly to the river system without treatment in the 2000s. Industry density is highest in the southwestern region (an old industrial zone) followed by the southeastern region (a new industrial zone). The highest density of roads occurs in the northwestern region (Fig. 1).

2.2. Sample collection and physicochemical analysis

A total of 30 surface sediments (0–10 cm) were collected from the middle of the river channel in March to April 2017 (Fig. 1). The sampling was designed to provide a relatively uniform sample distribution across the study area (Fig. 1). We used a GPS to record coordinate information (World Geodetic System-1984) for each site. Samples were collected using a clamshell bucket sampler and a composite sample from multiple grabs at each location was stored in a clean polyethylene bag and transferred immediately to the laboratory. Samples were stored in a cryogenic freezer. Large debris was removed (e.g., stones, wood), and the samples were crushed and passed through a 150-mesh (106 μm)

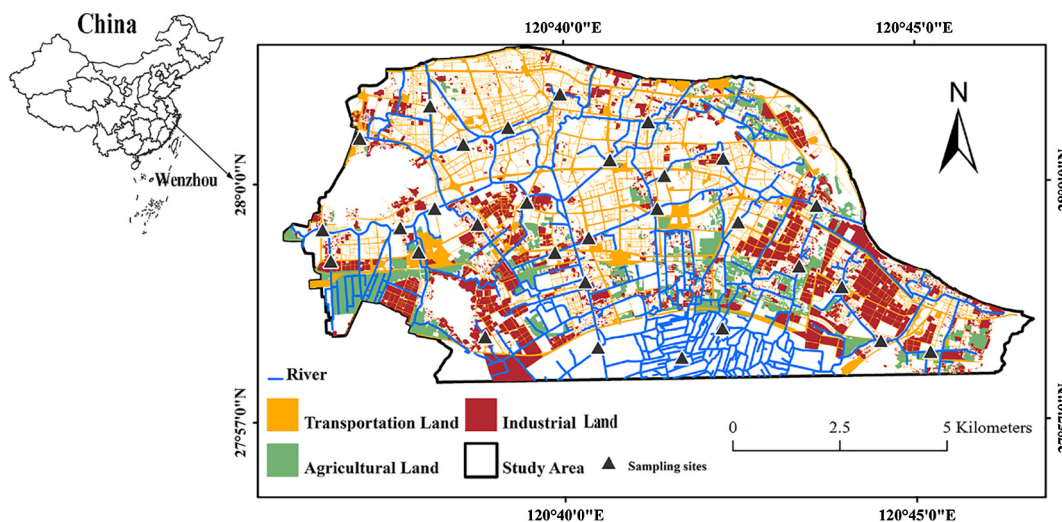


Fig. 1. Sampling sites and major land-use units in the Wen-Rui Tang River watershed.

nylon sieve. All samples were quartered to provide representative subsamples for further physicochemical analysis.

Total metal concentrations for Mn, Cu, Pb, Zn and Cd were determined on a 0.5 g sediment sample digested with mixed acids ($\text{HNO}_3\text{-HCl-HF-HClO}_4$) (USEPA, 1996). Metal concentrations in the digests were quantified using an atomic absorption spectrophotometer with a graphite furnace (Cd, Pb) (Agilent 8800 ICP-MS, Agilent Technologies; detection limit: Pb = 0.005, Cd = 0.01 mg L^{-1}) or by flame (Cu, Zn, Mn) (PinAAcle 900, Perkin Elmer; detection limit: Cu = 0.01, Zn = 0.01, Mn = 0.016 mg L^{-1}). Based on Pourreza and Ghanemi (2009), the detection limit was calculated as 3 times the standard deviation of blank samples. Sediment samples were analyzed in duplicate and the relative standard deviation (RSD) of all duplicates was $\pm 5\%$. In addition, we used the GBW-07312 reference sediment from Chinese Academy of Geological Sciences for quality control and determined recoveries of total metal concentrations, which ranged from 89 to 107%. Total organic carbon (TOC) in sediment samples was determined by the potassium dichromate oxidation method (Lu, 2000). Sediment pH values were determined with deionized water (m:v = 1:5).

2.3. Data sources and statistical analysis

This study examined eight factors known to influence metal concentrations in riverine sediments (Table 1). Anthropogenic activity factors included densities of industry (DI), livestock (DL), service industries (DS), population (DP) and roads (DR), along with agricultural area (AG). Natural factors included sediment total organic carbon (TOC) concentration and soil type (ST). Soil data were derived from the 2005 soil map of Zhejiang Province. Land-use data came from the Land Use

Survey Project of Wenzhou (2005) having a spatial resolution of 0.5 m. Industrial, livestock and service industry pollution data were acquired from the first national pollution source survey of China. DP was calculated based on population data from the Wenzhou Statistical Yearbook published by Wenzhou Municipal Bureau of Statistics (WSB, 2010; Chen et al., 2016). DR was obtained using ArcGIS 10.0 to calculate the total length of roads within each administrative division/area. DI, DL and DS were calculated using the kernel density function in ArcGIS 10.0. AG was calculated within a 1-km straight-line buffer of the sampling sites. Continuous data were converted to categorical data using the Natural Breaks classification method in ArcGIS 10.0 to meet the data format requirements of GDM (Feng et al., 2013). The classification categories for all eight impact factors are listed in Table 1 and their spatial distributions are depicted in Fig. S1. To evaluate the efficacy of the GDM, results were compared with those determined by Spearman correlation analysis (SCA) and stepwise multiple linear regression performed with SPSS 21.0. All graphical images were produced with Origin8.0.

2.4. Enrichment factor

The enrichment factor (EF) is considered an effective tool to differentiate the metal source between anthropogenic and naturally occurring sources (Adamo et al., 2005; Chen et al., 2007; Franco-Uría et al., 2009). As Mn is widely selected for use as a reference element, we chose it as the normalizing element for determining EF-values (Awagu and Uduma, 2013; Loska et al., 1997). Other widely used reference metal elements include Fe and Al (Loska et al., 2003; Nyangababo et al., 2005). Following Taylor (1964), we defined the EF as the metal

Table 1
Classification of impact factors.

Impact factors	Classification category (L)						Units
	1	2	3	4	5	6	
DI	0–3.97	3.98–7.95	7.96–11.9	12.0–15.9	16.0–19.9		Per km^2
TOC	7.76–13.8	13.9–27.0	27.1–41.0	41.1–53.0	53.1–90.4		ppm
DS	0–14.8	14.9–29.6	29.7–44.4	44.5–59.2	59.3–74.0	74.1–88.8	Per km^2
AG	0–0.58	0.59–2.2	2.3–4.8	4.9–8.4			km^2
DL	0–0.56	0.57–1.12	1.13–1.68	1.69–2.24	2.25–2.80		Per km^2
DP	3126–5205	5206–10,467	10,468–12,644	12,645–18,896	18,897–32,868		Per km^2
DR	1.26–4.03	4.04–7.03	7.04–9.59	9.60–13.6			km/km^2
ST	Coating mud	Yellow soil	Cyanosis clay paddy				None

(C_M) to manganese (C_{Mn}) ratio divided by the background metal to manganese ($(C_M/C_{Mn})_{background}$) ratio:

$$EF = \frac{(C_M/C_{Mn})_{sample}}{(C_M/C_{Mn})_{background}} \quad (1)$$

EF values are interpreted as: $EF \leq 1.5$ (no modification); $1.5 < EF \leq 3$ (minor modification); $3 < EF \leq 5$ (moderate modification); $5 < EF \leq 10$ (severe modification); and $EF > 10$ (very severe modification) (Birch and Olmos, 2008). The metal background values were determined from the average values of hundreds soil samples collected from the Wen-Rui plain of Zhejiang Province (Wang et al., 2007).

2.5. The Geographical Detector Method (GDM)

GDM was used to analyze correlations among the four metals (Pb, Cd, Cu and Zn) and the eight anthropogenic and natural influencing factors recorded for each sediment sampling site, including interactions among the influencing factors. The method principle examines whether the spatial distribution of the dependent variable Y (metal concentration) and the independent variable X (anthropogenic/natural influencing factors) tends to be the same, as expressed by the following equation (Wang et al., 2010):

$$q = 1 - \frac{1}{NO^2} \sum_{i=1}^L N_i \sigma_i^2 \quad (2)$$

where q is the power determinant of each influencing factor for the metal concentration, N is the number of samples, N_i is the number of samples in each category, and L is the number of classification categories. The σ^2 is the variance of Y and σ_i^2 is the variance for each classification category Y . Expressions $q \in [0,1]$ and $q = 1$ indicate that Y is completely determined by X while $q = 0$ indicates there is no association between Y and X . The value of the q -statistic indicates that X explains 100% of Y and the q -statistic measures the association between X and Y , both linearly and nonlinearly (Wang et al., 2010).

The interaction detector for GDM can also be applied to investigate the interaction between any two factors (symbolized by \cap). If $q(X1 \cap X2) = q(X1) + q(X2)$, the factors are independent of each other; if $\text{Max}(q(X1), q(X2)) < q(X1 \cap X2) < q(X1) + q(X2)$, the factors bi-enhance each other, which means that the $X1$ and $X2$ joint risk ($q(X1 \cap X2)$) enhances the single risk ($X1$ or $X2$) but is smaller than the two individual risks added together. Similarly, $q(X1 \cap X2) > q(X1) + q(X2)$ indicates that the factors nonlinearly enhance each other. If $q(X1 \cap X2) < \text{Min}(q(X1), q(X2))$, the two factors nonlinearly weaken each other; while $\text{Min}(q(X1), q(X2)) < q(X1 \cap X2) < \text{Max}(q(X1), q(X2))$, indicates the factors uni-weaken each other (Wang et al., 2010). More details on GDM can be found at <http://www.geodetector.org/>.

3. Results

3.1. Descriptive statistics and assessment of metal pollution in sediments

The average pH of sediments was 7.15 (range: 6.63–7.91) and average sediment TOC was 25.8 g kg⁻¹ (range: 7.8–90.4). The descriptive statistics and EF values of the metal concentrations in sediments of the Wen-Rui Tang River watershed are summarized in Table 2. Median values for elemental concentrations in sediments followed a decreasing order of Zn > Cu > Pb > Cd. Mean levels of all the analyzed metals in sediments were much higher than the corresponding background values. The EF values based on total metal concentrations followed (mean and range): Cd (115.6 [2.24–1477]) > Zn (12.84 [1.89–55.2]) > Cu (6.01 [0.65–13.4]) > Pb (3.16 [0.74–13.3]). According to EF classification criteria, all of the metals demonstrate contamination by anthropogenic sources ($EF > 1.5$). Pb displayed moderate modification, Cu severe modification, and Zn and Cd very severe modification.

3.2. Spatial distribution of EFs

EF values for the 30 sampling points are displayed in Fig. 2 to show the spatial distribution of metals in sediments of the Wen-Rui Tang River watershed. In general, the EF values for Cu, Zn, Pb and Cd had similar distribution trends across the watershed. The highest EF values for all metals appeared in the southwestern regions having the highest density of industrial activities (e.g., electroplating, printing and dyeing, tanning, etc.). The EF values for Cu and Zn were also somewhat elevated in the northeastern region, an area with a high density of livestock and poultry farms. EF values for Cd were generally very high throughout the entire study area with most EF values indicating serious pollution levels. While sediment sampling sites with Pb exceeding a moderate pollution level were rare, these higher Pb concentrations were located in the northwestern and southwestern regions.

Overall, metals in sediments of the Wen-Rui Tang River watershed showed a distribution consistent with contamination from high density industrial areas, indicating that surface runoff and sewage discharge from factories caused high contamination levels of metals in the sediment. Areas of elevated Cu and Zn also appeared to be related to districts with a higher density of livestock and poultry farms, reflecting that Cu and Zn contamination levels were highest around livestock and poultry farms. Contamination by Cd was very serious throughout the watershed while Pb was relatively low, which means the waste residue and wastewater from industry contains higher Cd and lower Pb concentrations, while emissions from traffic mainly contained Pb.

3.3. Effect of single factors on metal concentration

3.3.1. Contribution of anthropogenic and natural factors to metal concentrations

Using the GDM, we assessed the impact of individual anthropogenic and natural factors that could possibly influence metal concentrations in

Table 2

Statistical summary of total element concentrations (mg kg⁻¹) and enrichment factors (EF) for heavy metal risk assessment in sediments ($n = 30$) from Wen-Rui Tang River watershed.

Wen-Rui Tang River watershed ($n = 30$)		Cu	Zn	Pb	Cd	Mn
Descriptive statistics	Mean	194	1589	138	30.5	779
	Median	180	759	89.4	1.84	146
	SD	125	1581	118	60.0	745
	Minimum	29.5	2623	35.9	0.34	450
	Maximum	434	7616	644	314	1071
	BGV ^a	32.7	109	38.4	0.17	759
EF	Range	0.65–13.4	1.89–55.2	0.74–13.3	2.24–1477	
	Mean \pm SD	6.01 \pm 3.9	12.8 \pm 12.7	3.16 \pm 2.55	115.6 \pm 288.7	

^a Background value (BGV) compiled from Wang et al. (2007).

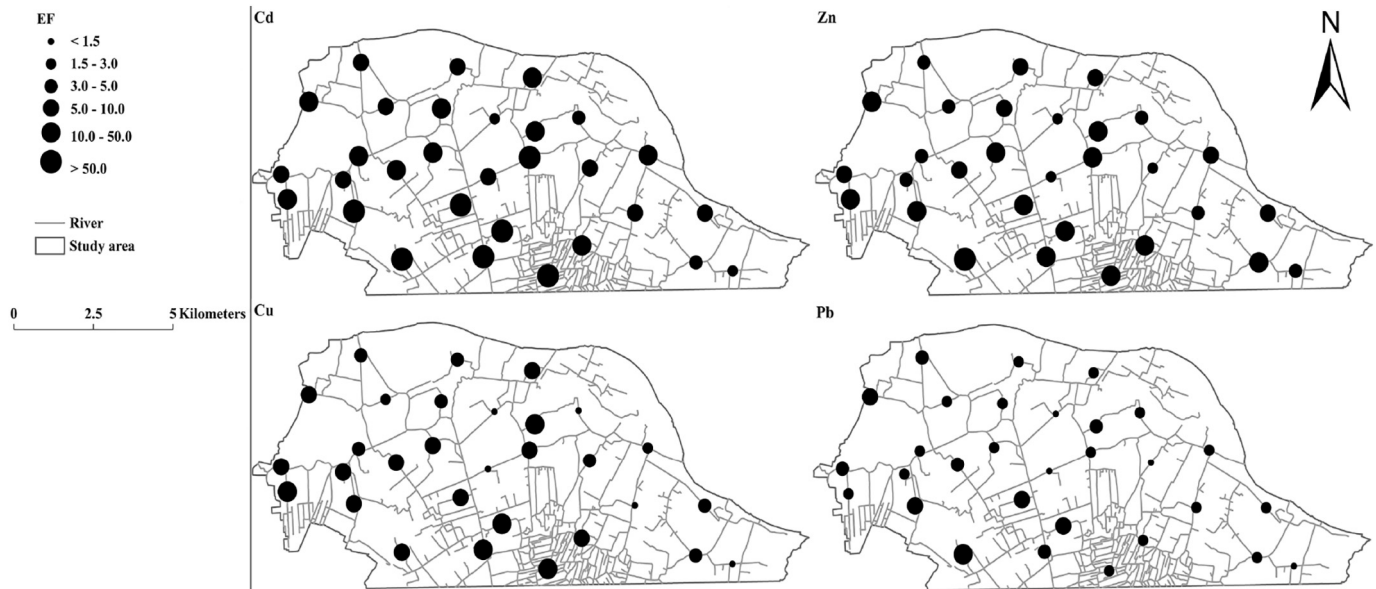


Fig. 2. Spatial distribution of EF for Cd, Cu, Zn and Pb in sediments of Wen-Rui Tang River watershed.

sediments of the Wen-Rui Tang River watershed (Fig. 3). The highest q -values (Zn = 0.676, Cd = 0.883, Cu = 0.35 and Pb = 0.781) were found for DI, which suggests that industry was the dominant factor causing metal pollution in the study area. Concentrations of Zn, Pb and Cd also showed a moderately strong influence from ST (q -value = 0.346). Compared to the other metals, Cu and Pb showed a somewhat stronger influence from DR (q -value of 0.309, and 0.356). All the other influencing factors showed a low level of potential contribution (<0.3) with TOC having a weak, but consistent contribution for all metals.

In summary, DI was identified as the primary factor contributing to metal concentrations in the riverine sediments. ST also showed a moderate secondary influence on Zn, Pb and Cd, but not for Cu. The contribution of DL to Zn and Cu was appreciably different from Cd and Pb, suggesting that Zn and Cu in livestock feed/manure maybe an important source of these metals. Compared to the other metals, Cu showed a stronger influence from AG, suggesting that farm chemicals

(e.g., pesticides/fertilizers) or livestock feeds/manure maybe potential Cu sources. Further, the contribution of DR to Cu and Pb was appreciably higher than for Cd and Zn, which suggests that traffic sources may have an influence on these metals. These GDM results further verify the spatial distribution of EF values presented in Section 3.2.

3.3.2. Comparison between GDM and SCA

We used Spearman correlation analysis (SCA) to validate the reliability of the GDM results (Table 3) and used Cu as a specific example to compare the differences between the GDM and SCA approaches (Fig. 4). DI ($r = 0.475$ – 0.528) showed significant correlations with all metals (Table 3). TOC (with Zn and Pb) and DL (with Cu) also showed significant correlations, but the correlations were weaker ($r < 0.400$) than those for DI. AG showed the lowest correlation with all metals, which was similar to the GDM result. However, the relatively high contribution of AG to Cu was not identified as for GDM (Fig. 3). The SCA

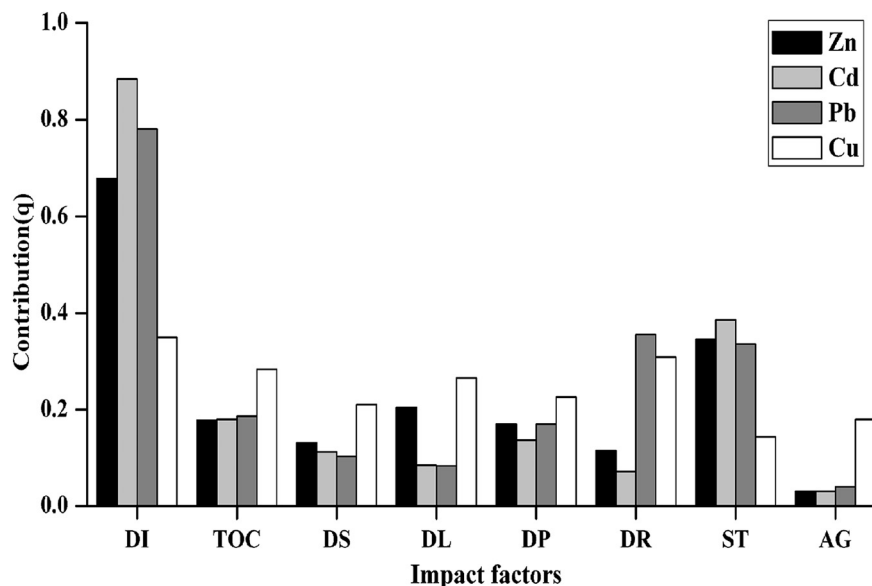


Fig. 3. Contribution of anthropogenic and natural factors influencing heavy metal concentrations.

Table 3

Spearman correlation analysis of eight anthropogenic and natural metal influencing factors with Cu, Zn, Pb and Cd concentrations.

Impact factors	Cu	Zn	Pb	Cd
DI	0.475**	0.513**	0.528**	0.517**
TOC	0.360	0.398*	0.378*	0.138
DS	-0.198	-0.279	-0.242	-0.226
DL	0.365*	0.294	0.170	0.154
AG	0.072	0.048	-0.009	0.046
DP	-0.225	-0.302	-0.186	-0.198
DR	-0.310	-0.178	-0.043	-0.037
ST	0.340	0.329	0.244	0.199

** Significance at $p \leq 0.01$ level (bilateral).

* Significance at $p \leq 0.05$ level (bilateral).

results were similar to those of the GDM analysis in identifying DI as an important contributor to metal pollution in the Wen-Rui Tang River sediments.

Fig. 4 comparing the GDM and SCA results revealed that both methods were consistent in identifying DI as a strong primary factor, and TOC and DL as secondary factors influencing sediment Cu concentrations. However, SCA and GDM deviated in their assessment of the other factors, with SCA indicating three negative q-values (DS, DP, DR) versus positive q-values from GDM. Overall, SCA verified the primary drivers of Cu concentrations in riverine sediments identified by GDM, but the influence of the weaker drivers showed some rather large differences. The differences between GDM and SCA results were virtually the same for Zn, Pb and Cd (Fig. S2).

3.4. Multi-factor analysis of metal concentrations

3.4.1. Multiple linear regression

Table 4 shows the results of multiple linear regression analysis for exploring anthropogenic and natural factors affecting sediment metal concentrations. This analysis found DI and TOC as significant variables ($p < 0.01$) for predicting metal concentrations. DI was a significant variable for all metals, while TOC was a significant variable associated with Zn and Pb concentrations. Collectively, these results indicate that Cd was primarily influenced by industry, while Cu, Zn and Pb were derived from industry with an influence from the TOC content of the sediment.

Table 4

Multiple regression equations for heavy metals with significant influencing factors.

Heavy metals	Regression equation	R^2	p
Cu	$17.7DI + 1.9TOC$	0.57	<0.01
Zn	$459.7DI + 26.9TOC$	0.72	<0.001
Pb	$38.1DI + 1.8TOC$	0.75	<0.001
Cd	$20.5DI$	0.71	<0.001

3.4.2. Interactions among anthropogenic and natural factors

Table 5 shows the interactions between anthropogenic (DI, DR) and natural factors (ST, TOC) that were previously identified as having a significant impact on sediment metal concentrations. All paired factors had higher predictive ability than any individual factor alone. This indicates that anthropogenic and natural factors enhanced each other in controlling metal concentrations in sediments. The relationship between ST and TOC was characterized as a non-linear enhancement, which meant that the summed contributions of TOC and ST were less than that of the interaction contribution between them. Similarly, non-linear enhancements were found for DR interactions with ST and TOC, and DR and DI interactions with Pb. However, most interaction contributions were less than the summed contributions of the individual factors. For example, DI interactions with ST and TOC were found to bi-enhance each variable's contribution for all metals, which indicates they were higher than for each individual factor alone.

4. Discussion

4.1. Source of metal pollutants

Previous studies demonstrated that elevated metal concentrations in river sediments originated mainly from anthropogenic activities rather than natural sources (Song et al., 2012; Bednarova et al., 2013). Based on the EF and GDM results of this study, the metals (Pb, Cd, Zn and Cu) in sediments of the Wen-Rui Tang River watershed were also attributed primarily to anthropogenic sources. The spatial distribution of EF for all metals showed that metals were seriously influenced by anthropogenic activities in the old industrial zone (southwestern region) but not in the new industrial zone (southeastern region), which was similar to the findings of Song et al. (2012), and might be due to stricter

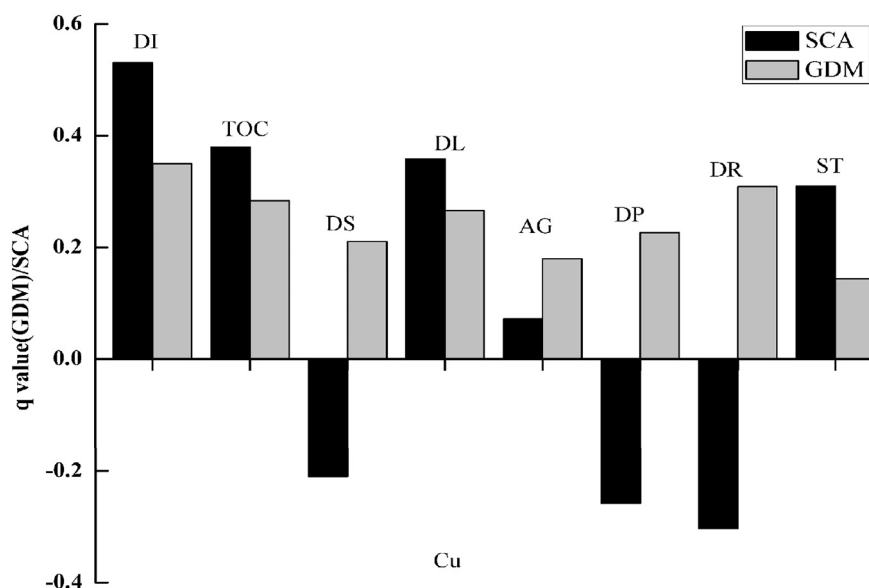


Fig. 4. Comparison of Geographical Detector Method and Spearman correlation results for Cu with its impact factors.

Table 5
Interaction between anthropogenic and natural factors for Cu, Zn, Pb and Cd.

Cu/Zn/Pb/Cd	DI	DR	ST
DR	0.67(†)/0.76(†)/0.87(††)/0.91(†)		
ST	0.44/0.82/0.70/0.89(†)	0.48/0.65/0.74/0.87(††)	
TOC	0.61/0.82/0.92/0.92(†)	0.65/0.49/0.43/0.48(††)	0.62/0.75/0.78/0.90(††)

Note: “†” represents the two factors enhance each other. “††” represents a non-linear enhancement of two factors.

management and environmental protection systems in the new industrial zone.

GDM analysis ascribed the primary anthropogenic factors contributing to metal pollution as DI and DL. In particular, DI was identified as having the strongest contribution to riverine metal concentrations. These results are consistent with the findings of Pan and Wang (2012) and Xiao et al. (2015) who found that industrial production in coastal cities of China often leads to increased metal contamination. In urban areas, metals associated with industrial wastes and automobile exhaust emissions are often attached to sediment/dust particles that are transported to waterways by atmosphere deposition and/or surface runoff/erosion due to the impervious nature of urban landscapes (Li et al., 2001; Bai et al., 2017). Thus, contaminants containing metals are transported to nearby streams where they can become part of the riverine sediment column (Lindström, 2001). In the Wen-Rui Tang River watershed, many factories currently and historically discharged industrial wastewater directly into the river system without any treatment (WEPP, 2014). Common industries within the watershed, such as electroplating (Cd, Zn) (Shomar, 2009) and printing/dyeing (Pb, Cd) (Federation, 2008), are known dischargers of metals. Therefore, the results obtained by the GDM were consistent with expectations for metal sources based on industrial use and deemed reliable for identifying the major watershed sources.

Chen et al. (2016) found that water quality in the Wen-Rui Tang River watershed was affected by agricultural land. According to GDM analysis, agricultural land use had a significant influence on Cu in sediments of the study area. Fertilizers, metal-containing pesticides/fungicides, and livestock feeds/manure are the primary sources of metal pollution (Cu) from agricultural lands (Marrugo-Negrete et al., 2017; Sun et al., 2013; Lu et al., 2012). Metals in agricultural lands are predominantly transported to surface waters through runoff/erosion processes; however, groundwater may also contribute metals in some cases (Qiao et al., 2017).

The GDM results further showed that the contribution of DL to Cu and Zn enrichment of riverine sediments was greater than for Pb and Cd. Previous studies reported that animal wastes generated by livestock and poultry breeding often have elevated Cu and Zn concentrations due to metal supplements added to livestock feeds (Meng et al., 2018). Usually, erosion of sediments associated with roadways and nearby soils is also a known source of metals (Hjortenkrans et al., 2006). In particular, Cu originating from vehicle brakes and Pb originating from fuel combustion are major metal sources associated with roads (Hjortenkrans et al., 2006; Arditsoglou and Samara, 2005). However, most industrial areas are in the suburbs where roads are usually less dense, to some extent concealing the effects of road density to the metal pollutions. Therefore, DR had a positive reinforcement influencing the interactions with other factors (such as DI, ST and TOC) on metal contamination in the river sediments in this study.

The GDM interaction detector indicated that metal concentrations in riverine sediments were affected by multiple anthropogenic and natural factors that produced a nonlinear enhancement interaction. Non-linear enhancement of ST and TOC was identified for all metals highlighting the importance of the metal binding capacity of soil materials as influenced by organic matter and other soil properties, such as pH, texture, and mineralogy. Low pH can increase the solubility of metals (Waterlot et al., 2011), which may enhance metal mobilization from terrestrial sources (Chen et al., 2011) and their subsequent retention

in the riverine sediments. TOC content is closely related to the behavior of metals in the aquatic environment, and previous studies have shown a significant positive correlation between metal pollution in urban estuary sediments and the TOC content of the sediments (Seidemann, 1991; Ünlü and Alpar, 2015). Organic matter has an especially strong affinity for Cu, which was demonstrated by the GDM results (Fig. 3). In contrast, the interaction of DI with DR, ST and TOC produced an additive rather than nonlinear enhancement in influencing metal concentrations of river sediments. Overall, the spatial distribution of metals in sediments was assessed by GDM to result from a combination of anthropogenic and natural factors (namely DI, DR, ST, TOC) that were interactive rather than mutually independent.

4.2. Comparison between GDM and other statistical methods

While Qiao et al. (2017) used Spearman correlation analysis (SCA) to verify the reliability of the key factors identified by the GDM, they did not compare the advantages and disadvantages of the two approaches. The results of comparative analysis between GDM with Spearman correlation and multiple regression methods in this study indicated that GDM was an effective method for identifying the contribution of anthropogenic and natural factors to metal concentrations in sediments. The Spearman analysis examined linear relationships between metal concentrations and potential impact factors. The positive and negative Spearman correlation coefficients indicated that there were both positive and negative correlations between metal concentrations and various influencing factors. A distinct advantage of the GDM analysis was that the method not only assessed linear relationships, but also nonlinear relationships. That is, the relevance between the metals and impact factors was examined and there was no positive or negative distinction, because the results were reported as values between 0 and 1 (Wang et al., 2010). If Spearman's correlation coefficients were not significant, it can only be concluded that no linear relationship existed between sediment metal concentrations and the influencing factors. However, Spearman's correlation was not able to detect potential nonlinear relationships. Therefore, the GDM has an important advantage compared to SCA in being able to detect both linear and nonlinear relationships among metal concentrations and potential influencing factors.

Both GDM and stepwise multiple linear regression can be used to estimate the contributions of various source factors to metal concentrations in riverine sediments (Atgin et al., 2000; Qiao et al., 2017). Stepwise multiple linear regression was mainly used to explore factors that had significant effects on metal concentrations in sediments and to exclude factors that had no apparent significant effect. If a significant model is generated, it can then be used to predict metal concentrations in sediments (Liao et al., 2017). The GDM has advantages compared to multiple linear regression in being able to measure spatially stratified heterogeneity. This refers to the phenomena that are more similar within strata than between strata, such as land-use types and climate zones, which are ubiquitous across spatial data (Wang et al., 2016; Zou et al., 2011). Additionally, GDM can assess all the interactions (e.g., linear and nonlinear, synergist vs antagonistic) between potential impact factors. In summary, GDM provides several unique data query abilities that makes it a valuable tool to be used in combination with other statistical approaches for rigorously characterizing factors contributing to metal pollution at the watershed scale.

Our previous work utilized the GWR method to determine the influence of land-use type on metal pollution in riverine sediments in this region and identified industrial land use as an important factor affecting metal distribution in the region (Xia et al., 2018). These findings are fully consistent with the results of this study. However, our previous work only analyzed three kinds of variables (industrial land, agricultural land and ecological land), while this study included eight categorical and continuous variables providing a more rigorous investigation and interpretation of metal sources and watershed distribution. By using these two methods, we found that GWR is commonly used to determine the effects of spatial heterogeneity on the explanatory variables (Wheeler and Tiefelsdorf, 2005). In contrast, GDM is a new spatial analysis method that can be used to measure the effects of an explanatory variable's spatially stratified heterogeneity (Wang et al., 2016). In addition, GWR has limitations associated with multicollinearity and kernel bandwidth selection, and only works with continuous data (Comber et al., 2018). In contrast, GDM works with both categorical and continuous data and is not limited by multicollinearity.

However, GDM also has some limitations. For example, GDM cannot directly show a negative correlation between metal concentrations and various influencing factors, but we can integrate SCA or multiple regression methods to identify the negative value. And GDM has a potential drawback of producing different results when the interval defining the impact factors change, such as in defining different geographical areas (Shrestha and Luo, 2017). For determining the optimal classification method, Feng et al. (2013) suggested use of q and interactive q values as indicators of the effectiveness of discretization methods.

5. Conclusions

Average EF values for Cu, Pb, Zn and Cd in Wen-Rui Tang River sediments indicated high levels of metal contamination that followed $Cd \gg Zn > Cu > Pb$. The spatial distribution of EFs demonstrated high contamination for all metals in the southwestern region of the watershed where historic industrial activities were concentrated. Due to stricter management and environmental protection regulations in the new industrial zone (southeastern region), metal concentrations are considerably lower than those found in the older industrial areas (southwestern region). Sediment concentrations of Cu and Zn were also elevated in the northeastern region, an area with higher levels of livestock and poultry production. Source apportionment based on GDM confirmed the spatial analysis attributing Cd enrichment primarily to industrial activities; Cu and Zn contamination to industrial activities and livestock and poultry production; and Pb and Cu pollution to industrial activities and traffic sources. Additionally, the GDM interaction detector revealed additive and nonlinear enhancement interactions between soil properties (TOC and ST) and anthropogenic activities with respect to metal enrichment. In comparison with other analysis of correlation, multiple linear regression analysis and GWR, GDM demonstrated distinct advantages of being able to determine both single factor and interactions among multiple factors (e.g., linear vs nonlinear, synergist vs antagonistic) without multicollinearities. These results from the GDM analysis provide a more comprehensive understanding of metal spatial distributions and the significant contributing factors at the watershed scale, which provides an important tool for environmental and water resource agencies to develop sustainable environmental management and remediation strategies.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.10.424>.

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