Quantifying influences of interacting anthropogenic-natural factors on trace element accumulation and pollution risk in karst soil

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HIGHLIGHTS

• Land use and smelting industry are most responsible for enhancing the natural factor.
• Anthropogenic+natural factors show nonlinearly enhanced effects on the trace elements.
• Interactive effect of land use+watershed explains 56% of the karstic soil Cd content.
• Interactive effect of land use+watershed explains 51% of karstic pollution risks.

GRAPHICAL ABSTRACT

ABSTRACT

This study quantified influences of interactions between anthropogenic and natural factors on trace element accumulation and pollution risk in karst soils at regional and local scales and identified the dominant interacting factors. A total of 513 soil samples were collected from Hechi, southern China to measure concentrations of arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb), which were compared with published background values. Descriptive statistics and occurrence characteristics were developed with geostatistical methods and the comprehensive pollution risk was calculated using the Nemerow pollution index (NPI). Geo-detector models were used to further examine and quantify the influence of 14 factors (5 anthropogenic and 9 natural) on trace element concentrations and NPI, both individually and interacting with the other 13 factors. The results clearly demonstrate that anthropogenic factors interact with natural factors to enhance nonlinearly and significantly trace element accumulation in karst soils. Watershed was the natural factor that most enhanced trace element accumulation when interacting with anthropogenic factors. Land use and smelting industry were the anthropogenic factors that most enhanced trace element accumulation when interacting with natural factors. Land use-watershed interaction accounted for 56% of Cd accumulation and smelting industry-watershed interaction for 19% of As accumulation. Land use-watershed, land use-lithology, and pH-watershed interactions...
1. Introduction

Pollution of soils by trace elements is an urgent problem throughout the industrialized world (Li et al., 2013; Kong, 2014) and quantifying the accompanying risks poses a major challenge to regulators (Lu et al., 2015). Karst soils are particularly problematic because the unique hydraulic and hydrogeological characteristics of karst areas render them highly vulnerable to pollution from human activities. There are many studies on the unilateral effects of anthropogenic or natural factors (Reimann and de Caritat, 2005; Nanos and Martín, 2012; Lv et al., 2013; Ding et al., 2017). Common anthropogenic factors include land use (Xia et al., 2011; Zhao et al., 2012; Kuusisto-Hjort and Hjort, 2013; Cutillas-Barreiro et al., 2016), tailings ponds (Romero et al., 2007; Rodríguez et al., 2009), industrial and mining activities (Li et al., 2014; Yan et al., 2015; Shen et al., 2017), and chemical industries (Dragović et al., 2014; Cutillas-Barreiro et al., 2016)). Natural factors include pH (Zeng et al., 2011), topography (i.e., elevation and slope) (Lv et al., 2013; Ding et al., 2017), hydrology (Zhao et al., 2012; Ding et al., 2017; Qiao et al., 2019a), and parent material lithology (Taghipour et al., 2011; Lv et al., 2013). In contrast, little is known about how anthropogenic and natural factors interact to influence trace element accumulation in karst soils. However, some recent studies suggest that natural factors coupled with human activities may enhance trace element accumulation in karst soils (Luo et al., 2019; Qiao et al., 2019b).

To characterize interactive influences, traditional multivariate analyses (Taghipour et al., 2011) and other statistical methods have been widely applied. Examples include correlation analysis (Xia et al., 2011; Kuusisto-Hjort and Hjort, 2013), principal component analysis (Mamat et al., 2014; Zhou and Wang, 2019), cluster analysis (Dragović et al., 2014; Mamat et al., 2014), and multivariable logistic regression models (Hill et al., 2008; Wu et al., 2010). However, there are three limitations to applying traditional statistical models to calculate interactive influences. First, the multivariate logistic regression model and multivariate analysis method require a stochastic field and numerical data to meet the homoscedasticity assumption (Christakos, 2010). Second, the interaction of two factors on trace element accumulation in soil can have multiple coupling forms, whereas conventional linear regression models are limited in examining only two-variable multiplication. Finally, traditional spatial interactive models are created using spatial local variables, lacking predictive power for the larger-scale variability of influences because of the spatial stratified heterogeneity within variables (Pearce et al., 2011; Wang et al., 2016).

The geo-detector model overcomes these limitations, with the advantages of no assumption of linearity and not being influenced by the collinearity of multivariables. Geo-detector is a spatial variance analysis tool used to detect nonlinear relationships between geographical factors. It can manage quantitative and nominal variables, and apreempts of this study, identifies dominant factors in a group, and quantifies the interaction between two different factors. The geo-detector method was proposed by Wang et al. (2010, 2016) to detect risk factors for neural tube defects. It has been widely used to assess the influence of individual and interacting factors affecting environmental problems, such as antibiotic soil pollution (Li et al., 2013), groundwater contamination (Zhu et al., 2019), trace element soil pollution (Shi et al., 2018; Wang et al., 2018; Qiao et al., 2019b; Luo et al., 2019), and soil erosion (Gao and Wang, 2019).

This study used geo-detector modeling to investigate individual anthropogenic and natural factors and to quantify the influence of their interactions on the accumulation of arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb) in soil and the associated risk. Hechi city in south China was chosen as the study area for its distinct human environment (many industrial and mining activities, various land uses, and endemic diseases) and its complex geology (karst terrain with complex hydrogeology, abundance in natural resources, and frequent natural disasters). The objectives of this study were three-fold; (1) measure concentrations of 5 trace elements (As, Cd, Cr, Hg, and Pb) and compare with known background concentrations, in order to quantify the degree of accumulation in soil and calculate the comprehensive pollution risk, (2) quantify the individual and interactive influences of factors impacting trace element levels at at regional and local scales, and (3) identify the dominant individual factors and specific interactions between two factors affecting trace element accumulation and pollution risk. The results from this study reveal the most important stand-alone factors and interactions of factor pairs governing trace element accumulation and pollution risk in karst soils and will inform regulators about specific strategies to reduce trace element accumulation.

2. Materials & methods

2.1. Study area

Hechi city, located in the Guangxi Zhuang Autonomous Region (Fig. 1a), is one of the largest karst areas in China and is known as the “land of non-ferrous metals”. This area belongs to the circum-Pacific polymetallic metallogenic belt with abundant mineral resources (Huang et al., 2012). Smelting and mining activities, and discharges from chemical industries are the primary sources of pollution (Yuan et al., 2017). Monitoring data from the local environmental protection agency have identified As, Cd, Cr, Hg, and Pb as the primary trace elements being released by human activity and contaminating soils in the region. Four counties in Hechi (Fig. 1b) with a total area of approximately 13,458 km² were selected for this research, Nandan (3902 km²), Jinchengjiang (2340 km²), Huanjiang (4558 km²), and Luocheng (2658 km²). According to the socio-economic statistics from the Hechi Department of Statistics in 2013 (Hechi Editorial Committee of Statistical Yearbook, 2014), Nandan is dominated by secondary industries (62.2%), Jinchengjiang is dominated by secondary (43.3%) and tertiary (44.4%) industries, and Huanjiang and Luocheng have industrial structures in a relatively balanced state.

2.2. Soil sampling & chemical analyses

A total of 513 soil samples were collected on a regular grid with a 5-km center (Fig. 1b). Soil samples were collected from the ground surface to a depth of 20 cm during a 3-month period in 2013. Five subsamples were taken from each cell, four from the vertices (3 m × 3 m) and one from the center, which were then mixed together to create a composite sample. Every cell was sampled and all samples were recorded using GPS. Also, 5% of the samples were selected randomly for quality control. The soil samples were air dried, ground, and divided into two parts. One part was passed through a sieve with 2-mm apertures for pH measurement, and the other part was passed through a 100-mesh sieve and then digested with HNO₃/HF-HClO₄ in a Teflon digestion vessel. The pH of each soil sample was measured directly in a slurry with a soil: water ratio of 1: 2.5 (m:v) with a pH meter (PB-10, Sartorius Instruments, Germany). As, Cd, Cr, and Pb were analyzed with a PerkinElmer Optima 5300DV inductively coupled plasma-optical emission spectrometry (ICP-OES). Hg was analyzed using atomic fluorescence spectrometry (AFS-9130, JiTian Instruments, Beijing, China). The
national standard sample GSS-4 (GBW07404) from the National Research Center (Beijing, China) was used as a reference for analytical quality control.

2.3. Data sources & processing of factors

The organizational structure for modeling pollution risk, trace element accumulation, factor categories and individual factors (explanatory variables) is shown in Fig. 2. The comprehensive pollution risk posed by the concentrations of all 5 trace elements from the 513 soil samples was calculated using the Nemerow pollution index (NPI). Based on a thorough literature review and investigation of the study area, a total of 14 factors (5 anthropogenic and 9 natural) influencing trace element accumulation were selected for study (Fig. 2). The 5 anthropogenic factors and the symbols used were land use (A1), tailings (A2), smelting industry (A3), chemical industry (A4), and mining industry (A5). The 9 natural factors and the symbols used were coal (N1), ferrous ore (N2), non-ferrous ore (N3), limestone (N4), pH (N5), slope (N6), elevation (N7), watershed (N8), and lithology (N9).

A tool in ArcGIS (version 10) called ExtractMultiValuesToPoints was used to integrate the attribution of the 14 factors. Prior to spatial overlay, the data of the factors were geometrically rectified and projected into Xian_1980 coordinates. The numerical data for individual factors were first transformed into categorical data and then entered into the geo-detector models.

2.3.1. Anthropogenic factors

Fig. 3 shows maps of the study area with the spatial distribution of anthropogenic factors influencing trace element accumulation. The 30-m resolution 2015 land-use dataset used was obtained from the Data Center for Resources and Environmental Sciences, Chinese Academy of Sciences (RESDC) (http://www.resdc.cn) (Ning et al., 2018). Types of land use included cropland, forestland, grassland, and construction land (Fig. 3a). The cropland area was approximately 1631.88 km², comprising 12.2% of the study area, whereas forestland, grassland, and construction land made up 71.0%, 16.3%, and 0.5% of the study area, respectively. Fig. 3c shows the locations where tailings and mining, smelting, and arsenic industries are located. The Euclidean distances from each sampling location (Fig. 1b) to the locations of all these anthropogenic factors were divided into 2 stratifications using ArcGIS 10.0, surrounding areas (distance ≤ 5 km) and remote areas (distance > 5 km).

2.3.2. Natural factors

Fig. 3 also shows maps of the spatial distribution of the natural factors influencing trace element accumulation. Mineral resources in the study area (Fig. 3d) include coal, non-ferrous ore, ferrous ore, and...
limestone. The Euclidean distances from each sampling location to the locations of all these mineral-resource factors were divided into 2 stratifications, surrounding areas (distance ≤ 5 km) and remote areas (distance > 5 km). The cut points of pH to each sampling site was obtained from the Chinese Environmental Quality Standard for Soils (GB 15618-1995), which divides pH into 4 stratifications; strong acidity (pH ≤ 5.5), weak acidity (5.5 < pH ≤ 6.5), neutral pH (6.5 < pH ≤ 7.5), and alkaline (pH > 7.5), as shown in Fig. 3b. A 30-m resolution digital elevation model (DEM) was also acquired from RESDC. Elevations were generally higher in the northwest and lower in the southeast. The difference between the highest point (1688 m) and lowest point (86 m) was approximately 1.6 km. The
elevations were split into 7 stratifications by the natural break method with cut points of 240, 330, 420, 520, 640, and 780 (Fig. 3e). Slopes were calculated from the DEM and split into 5 stratifications (Fig. 3f), with cut points of 2, 6, 15, and 25 based on Technical Regulations for Land use Investigation in China (1984). The study area was split into 8 sub-watersheds (Fig. 3g), using the DEM using the Hydrology toolset in ArcGIS 10.0.

A 1:200,000 geological map of Guangxi was acquired from the geological cloud platform (http://geocloud.cgs.gov.cn/). The map was georeferenced and clipped to fit the study area (Fig. 3h) and then digitized to create vector layers with Xian_1980 coordinates in ArcGIS 10.0 for further analysis. Lithology was split into 6 categories; metamorphic rock, magmatic rock, clastic rock, carbonate rock, clastic rock intercalated with carbonates, and carbonate rock intercalated with clastics. Water storage capacity (WSC) was also considered. Carbonate rock was split in two categories: Carbonate Rock 1 with a high WSC and Carbonate Rock 2 with a low WSC (Fig. 3h). Metamorphic, magmatic, clastic, and clastic rock intercalated with carbonates were assigned a low WSC, and carbonate rock intercalated with clastics a moderate WSC.

2.4. Calculations, analyses, & modeling

2.4.1. Nemerow pollution index (NPI)

The NPI is defined in Eq. (1) (Nemerow, 1974):

$$\text{NPI} = \sqrt{\frac{(P - 1)^2 + (P_{\text{max}} - 1)^2}{2}}$$

where $P = \frac{1}{n} \sum_{i=1}^{n} P_i$ represents the mean NPI value, $P_i$ for each trace element, $n$ is the total number of trace elements (5), and $P_{\text{max}}$ represents the maximum value of $P$. The NPI value for each trace element ($P_i$) is quantified by the relationship $P_i = C_i/S_i$, where $C_i$ is the concentration measured, and $S_i$ is the maximum allowable concentration in soil for each trace element, $i$, established by regulators (Nemerow, 1974).

2.4.2. Geostatistical analysis

Geostatistical methods with variography and kriging interpolation provide an unbiased estimate of the variables at unmeasured locations. This approach has been widely applied to model the spatial structure and variability of soil properties (Qishlaqi et al., 2009; Lv et al., 2013), and is based on fundamental assumptions concerning random variables, where the distances between observed points are plotted against their similarities to produce a semi-variogram. The semi-variogram function is described in Eq. (2):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (Z(x_i) - Z(x_i + h))^2$$

where $\gamma(h)$ is a semi-variogram that measures the mean variability at the distance, $h$, between the points $x$ and $x + h$, $N(h)$ is the number of pairs of sample points over the distance, $h$, and $Z(x_i)$ and $Z(x_i + h)$ are the sample values of the variable, $Z$, separated by the distance, $h$.

Eq. (3) describes ordinary kriging, the most common univariate interpolation method which uses semi-variograms to quantify the spatial variation of a regionalized random variable.

$$Z'(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i)$$

where $Z'(x_0)$ is the predicted concentration of trace element, $i$, at location $x_0$, $Z(x_i)$ is the measured concentration of trace element, $i$, at location $x_i$, $\lambda_i$ is the weight assigned to $Z(x_i)$, and $n$ is the total number of measurements. The cross-validation (leave-one-out) of ordinary kriging was used to assess accuracy. It removes each sampling site one at a time and then predicts the associated data value. The Root Mean Square Error (RMSE) is calculated using Eq. (4), when cross-validation comparing the measured and predicted values for all points. Low values of RMSE indicate high accuracy.

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (Z(x_i) - Z'(x_i))^2}$$

where $Z(x_i)$ and $Z'(x_i)$ represent the measured and predicted values, respectively, for each trace element, $i$, and $n$ is the total number of sampling sites.

All calculations and statistical analyses in this study were performed using SPSS 13.0. The geostatistical analyses and maps were generated with ArcGIS (version 10.0) and GS+ software.

2.4.3. Geo-detector modeling

Geo-detector modeling is used to identify the governing force of a responding variable under the assumption that variate X is associated with variate Y if their spatial pattern is consistent. This study used two common sub-modules: the factor detector and the interaction detector.

A factor detector was used to examine the individual influences of the 14 factors investigated on trace element accumulation in soil. It was assumed that X was the value of the anthropogenic or natural factor at the sampling sites and Y was the influence of that factor on accumulation of the trace elements in soil from the 513 locations sampled. The statistical value of $q_i$ can be used to test the influence of $X$ on $Y$, which was calculated using Eq. (5):

$$q_i = 1 - \frac{1}{N_i N_i^*} \sum_{i=1}^{N_i} N_i \sigma^2$$

where $q_i$ is an index value used to measure the spatial association between $X$ and $Y$, $i = 1, 2, 3, ..., L$, where $L$ is the number of strata (sub-regions or sub-classes) of factors $X$ and $N_i$, and $N_i$ are the numbers of samples in the study area and in each stratum, $i$, respectively (Wang et al., 2010; Wang et al., 2016). The symbols $\sigma^2$ and $\sigma^2_i$ present the variances of $Y$ in the global area and in each stratum, $i$, respectively. The value of $q_i$, $\in [0, 1]$, indicates how much $Y$ is influenced by $X$. The larger the value of $q_i$, the stronger the spatial association between $X$ and $Y$.

The interaction detector was used to examine the interactive influences of paired factors from the 14 factors modeled. The interaction detector determines whether two factors act independently of each other or whether their influences are weakened or enhanced when they co-exist, and is defined by the 5 scenarios described in Eq. (6):

$$q(A, B) = q(A) + q(B) - q(A) q(B)$$

The $q$ value of factors $A$ and $B$ calculated from the interaction detector can be described as $q(A)$ and $q(B)$, respectively. A new factor layer and sub-regions can be generated by spatially overlaying the $A$ and $B$ factor layers. The interaction types between two covariates are defined by comparing the interactive $q$ value of the factor pair considered with the $q$ value of each factor alone (Wang et al., 2010; Wang et al., 2016). The symbol $NI$ denotes the interaction between factors $A$ and $B$, and X1||Y2 is implemented by overlaying the two variables using GIS tools. The symbol $q(AB)$ denotes the $q$ value of $AB$. 
3. Results

3.1. Descriptive statistics & occurrence characteristics of trace elements

Table 1 lists the statistics for the raw, logarithmic-transformed, and semi-variance data for the trace elements. The coefficient of variation (CV), which is the ratio of mean to the standard deviation, was high for the raw As, Cd, and Pb data. To fit the semi-variance functions (Eq. (2)) of trace element concentrations, an exponential model was used for Cd, Hg, and Pb, and a Gaussian model was used for As and Cr. The range in values for all 5 trace elements was larger than the 5-km grid spacing. The largest range in value was 54 km for Cd, followed by 26 km for Cr. Table 1 also lists the background concentrations taken from Chinese Environmental Quality Standard for Soils (GB 15618-1995) and percentage of measurements exceeding the background concentrations for each trace element. The percent of concentrations exceeding background concentrations for As, Cd, Cr, Hg and Pb in the 513 samples was 42.7%, 51.9%, 21.3%, 73.9%, 62.0%, respectively. The descriptive statistics of NPI were calculated by Eq. (1) where the values of $S_i$ were taken from the background concentrations of each trace element.

Logarithmic transformation was used to normalize the raw data for the 5 trace elements and NPI prior to kriging and inverse logarithmic transformation was used after kriging due to the high skewness (Table 1). The spatial patterns of trace element concentrations and NPI values are shown in Fig. 4a–f. The spatial patterns of As, Cd, Cr, Hg and NPI were interpolated by ordinary kriging (Eq. (3)). The spatial pattern of Pb concentration was interpolated using the inverse distance weighted method because even logarithmic-transformed Pb data did not pass K–S normality test ($p < .01$). Cross validation showed that the RMSE (Eq. (4)) of As, Cd, Cr, Hg, Pb and NPI were 8.97, 0.36, 4.94, 0.06, 17.15 mg·kg$^{-1}$, and 1.34, respectively. Generally, areas with higher trace element concentrations were closer to construction land, sites of industrial and mining enterprises, near rivers, and in areas where the pH was relatively high. The distribution of As (Fig. 4a) was evenly distributed in the study area, compared with Cd, Cr, and Hg (Fig. 4b–d), which showed considerable spatial clustering. Concentrations of Pb (Fig. 4e) were relatively high in soil in Jinchengjiang, southeast Nandan and in central-northwest Huanjiang. The NPI map (Fig. 4f) showed clusters of high risk in Jinchengjiang, and near or on the boundaries between Nandan, Jinchengjiang, and Huanjiang.

3.2. Dominant individual factors on trace element accumulation

The individual impact of each factor on trace element accumulation was quantified using the q statistic values (Eq. (5)). The maximum q statistic value represents the dominant individual factor influencing the concentration of a trace element. Fig. 5 shows the maximum q statistics value for the 5 trace elements, for the entire study area and each county. For the entire study area, As concentrations were dominated by anthropogenic factor A3 (smelting industry), Pb concentrations by anthropogenic factor A5 (mining industry), Cd and Hg concentrations by the natural factor N8 (watershed), and Cr concentrations by the natural factor N5 (pH).

At the local scale the most important factors varied between the four counties. Anthropogenic factors A1 (land use) and A3 (smelting industry) were most influential in Nandan, whereas natural factors were more important in other counties. The governing factors were N3 (non-ferrous ore) and N9 (lithology) in Jinchengjiang, N5 (pH) and N8 (watershed) in Huanjiang, and N5 (pH) and N9 (lithology) in Luocheng. The anthropogenic factor (A3) was most influential for As in Nandan, but natural factors N3 (non-ferrous ore) and N5 (pH) were in the other counties. For Cd, anthropogenic factor A1 (land use) governed in Nandan, but natural factors N5 (mining industry), N8 (watershed), and N9 (lithology) did so in the other regions. Natural factors were most influential for Hg concentrations at all scales. For Pb concentrations, anthropogenic factors A1 (land use) and A3 (smelting industry) were dominant in Nandan and Huanjiang, whereas natural factors N3 (non-ferrous ore) and N9 (lithology) were dominant in Jinchengjiang and Luocheng.

3.3. Interactive effects of factors on trace element accumulation

Fig. 5 showed that the 3 most influential individual anthropogenic factors were A1 (land use), A3 (smelting industry), and A5 (mining industry) and the 4 dominant individual natural factors were N3 (non-ferrous ore), N5 (pH), N8 (watershed), and N9 (lithology). The interaction detector calculations (Eq. (6)) were used to determine how each of these 7 influential, stand-alone factors interacted with the other 13 factors. The maximum interactive q value among the 13 interaction results is plotted on the left side of the bidirectional bar graph in Fig. 6. On the right side of the bidirectional bar graph, the q value of the dominant factors and maximum interaction factor are added. Fig. 6 illustrates, most of the factor-pair interaction types of the interaction detector were nonlinearly enhanced (Eq. (6), scenario #5). Five interacting factor pairs exhibited an independent effect (Eq. (6), scenario #4), while N8/N9 in Huanjiang and N5/N9 in Luocheng showed bivariate enhancement (Eq. (6), scenario #3).

N8 (watershed) was the common interacting factor across the study area. For As and Cd accumulation, N8 (watershed) had an interactive effect with anthropogenic factors A1 (land use) and A3 (smelting industry). The land use/watershed interaction (A1/N8) accounts for 56% of Cd accumulation, and the smelting industry/watershed interaction (A3/N8) accounts for 19% of As accumulation. The main factors influencing Hg when interacting with other factors in the larger study area were N8 (watershed) and N9 (soil lithology). In Nandan, anthropogenic factors A1 (land use) and A3 (smelting industry) were nonlinearly enhanced by the natural factors, whereas the interactive effects of natural factors were controlling in the other three counties.

3.4. Interactive effects on comprehensive pollution risk

The diagonal in Table 2 are q values calculated from the interaction detector of 14 stand-alone factors on NPI. The individual factors had a

<table>
<thead>
<tr>
<th>Element</th>
<th>Raw data</th>
<th>Log transform</th>
<th>Semi-variance</th>
<th>Background concentrations (mg·kg$^{-1}$)/exceedance (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Mean</td>
<td>C.V.</td>
<td>Skewness</td>
<td>Kurtosis</td>
</tr>
<tr>
<td>Cd</td>
<td>1.47</td>
<td>2.80</td>
<td>9.15</td>
<td>123.09</td>
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<tr>
<td>Cr</td>
<td>68.27</td>
<td>0.83</td>
<td>2.25</td>
<td>9.83</td>
</tr>
<tr>
<td>Hg</td>
<td>0.48</td>
<td>1.50</td>
<td>5.20</td>
<td>39.84</td>
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<tr>
<td>Pb</td>
<td>76.06</td>
<td>2.50</td>
<td>8.50</td>
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<td>2.34</td>
<td>8.67</td>
<td>114.2</td>
</tr>
</tbody>
</table>

$^a$ Percentage of measurements exceeding the background concentrations.

$^b$ Not applicable.
minor influence on NPI in the study area due to local correlation and regional differentiation. A total of 91 \((C_i^2_a)\) pairs of interactive influences were calculated on NPI for the entire study area. A1 (land use), N3 (non-ferrous ore), N5 (pH), N6 (slope), N8 (watershed) and N9 (lithology) had the strongest interactive effects on NPI values. The interacting factor pairs land use \(∩\) watershed (A1 \(∩\) N8), land use \(∩\) lithology (A1 \(∩\) N9), and pH \(∩\) watershed (A1 \(∩\) N9) account for 51%, 19%, and 15%, respectively of the NPI values.

4. Discussion

4.1. Interactive effects on trace element accumulation

As shown in Figs. 5 and 6, the 14 factors acting alone, and in interaction with each other, caused significant accumulation of the 5 trace elements throughout the study area. When excess accumulation of pollutants in soils is caused by human activities, regulatory measures can be effective. Such measures will be ineffective if the dominant factors controlling accumulation are natural. Results from recent studies indicate that anthropogenic factors are having an increasing impact on trace element accumulation in soil (Liao et al., 2019; Qiao et al., 2019b; Luo et al., 2019; Shi et al., 2018).

The findings from this study show that anthropogenic factors can significantly interact with natural factors to nonlinearly enhance trace element accumulation in karst soils. Fig. 7 illustrates the interactive effects of the anthropogenic factors land use (A1) and smelting industry (A3) when paired with the other 13 factors on accumulation of 3 trace elements at different scales (i.e., some for the entire study area and some for individual counties). Land use (A1) (Fig. 7a–c) and the smelting industry (A3) (Fig. 7d–f) were the anthropogenic factors most responsible for enhancing trace element accumulation when paired with natural factors, especially non-ferrous ore (N3), pH (N5), slope (N6), watershed (N8), and lithology (N9). Modifying land use and better enforcing existing pollutant discharge limits for the smelting industry and/or lowering discharge limits should be considered by regulators.
The land use types in the study area include cropland, forestland, grassland, and construction land (Fig. 3a). Changing land use has the potential to alter the rate of accumulation of trace elements in soils, thereby impacting NPI (Kuusisto-Hjort and Hjort, 2013). For example, it is known that fertilizer application in croplands encourages the accumulation of Cd. From the statistical data available for industry in the study area, especially Nandan, secondary industries have grown extensively and land use for construction has expanded in recent decades, and forested areas have decreased significantly.

4.2. Interactive effects on NPI

The 3 factor pairs that interacted to yield the most influence on comprehensive pollution risk posed by the trace elements are listed in Table 3. Land use (A1), watershed (N8), pH (N5), and lithology (N9) had the strongest impact on trace element accumulation in soil when they interacted with other factors. The types of land use data included cropland (194 samples), forestland (232 samples), grassland (36 samples), and construction land (51 samples) (Fig. 3a). The mean NPI among the different land use types showed the following trend: construction land (9.41) > cropland (6.32) > forestland (6.28) > grassland (2.32), indicating that use of land for construction posed a higher pollution risk than the other three land uses. As RESDC describes, construction land includes urban-rural construction land and industrial-mining land, suggesting that policy makers should focus more on soil pollution surrounding industrial and mining lands in karst areas. Land use for grasslands, showed a very low NPI (2.32), and a t-test showed that the mean NPI of grassland type was significantly different from the other three land uses (p < .05).

It is clear from Table 3 that decision-makers should focus more on the watershed (N8) factor when considering pollution prevention and the control of trace element accumulation in karst soils. Hechi lies in the upper-middle Pearl River basin, which is the fourth-largest watershed with the second-largest discharge volume in southern China. Situated in a subtropical monsoon climate, the rainy season (May to September) is accompanied by acid rain, flooding, and geological disasters (Zhang et al., 2011). Recent research has demonstrated that the transportation of trace elements increases significantly during periods of heavy rainfall (Qiao et al., 2019a). During the flood season, pollutants adsorbed to solids in river sediment or released from flooding tailing ponds end up being deposited in floodplains and other surface soils, where it diffuses and/or is carried by infiltrating rainwater to the underlying soil. When flash flooding occurs in karst areas, contaminants are transported rapidly, and in some local areas directly into underlying aquifers. Karst aquifers are characterized by rapid groundwater flow in solution channels and fractures that do not confront the moving groundwater with significant porous material to retard contaminant migration via adsorption, large openings and fractures. Research has demonstrated that contaminants are rapidly flushed out of karst aquifers, where they enter rivers, and are then redistributed and redeposited onto surface soils (Zhu et al., 2019).

A t-test of NPI between eight watersheds in the study area (Fig. 3g) showed that the mean NPI in the Diaojiang sub-watershed (13.00) and the Dagou sub-watershed (10.61) were significantly higher (p < .05) than the other watersheds in the study area.
than that of the other six sub-watersheds (3.16–4.51). The Diaojiang sub-watershed has many smelter activities, which use non-ferrous ore as their primary raw material. The most abundant impurities in non-ferrous ore are As, Hg, and Pb. Fig. 5 shows that non-ferrous ore (N3) significantly affected the As, Hg, and Pb in Jinchengjiang where the Diaojiang river flows through. It therefore seems likely that the high pollution risk associated with the Diaojiang sub-watershed is partly related to the smelting of non-ferrous ore. As Fig. 4 shows, there are two high-value areas of Cd, Cr, and Hg accumulation and NPI in the Dagou sub-watershed which lies among Nandan, Huanjiang and Jinchengjiang. In addition, the Dagou sub-watershed is characterized by forestland, high pH, high elevation and slope, a high WSC of carbonate rock, and is known to have abundant limestone ore. It can therefore be inferred that the high pollution risk of the Dagou basin may be caused by underground-rivers.

As shown in Table 3, the land user/lithology (A1*N9) interaction accounted for 19% of the spatial pattern of NPI. A t-test of the 7 lithology types (Fig. 3h) showed that the mean NPI of carbonate rock 1 (9.26) and carbonate rock 2 (8.98) had significantly higher (p < .05) NPI values than metamorphic, magmatic, and clastic rock, and carbonate rock intercalated with clastics (1.47–4.71). The mean NPI of metamorphic (1.72) and magmatic rock (1.47) were significantly lower than the others. These results show that carbonate rocks were the lithology most influencing the observed trace element accumulation in karst soils in the study area, and we recommend that policy makers consider underlying lithology as having a significant impact on NPI in soils.

As shown in Table 3, the pH/watershed (N5*N8) interaction accounted for 15% of the spatial pattern of NPI. The mean NPI values in soils from the areas with the 4 different pH categories (Fig. 3b) followed the trend: alkaline (11.08) > neutral pH (8.58) > weak acidity (5.20) > strong acidity (3.47). A t-test showed that soils having a strong acidity had significantly lower mean NPI values than that of the other three classes (p < .05). The pH plays an important role in determining the solubility and activity of trace elements in soil (Hernandez et al., 2003; Zeng et al., 2011), and affects which chemical species trace elements form and their solubility (Chen et al., 2011). All 5 of the trace elements in this study were metals or metalloids, which tend to be more soluble in soils with lower pH (Liu et al., 2015). Therefore, soils with low pH encourage leaching of trace elements and have less accumulation. It is recommended that policy makers consider pH as an important factor influencing trace element pollution risks in soils.

4.3. Occurrence characteristics & dominant factors

The dominant factors and corresponding maximum q statistics values (Fig. 5) clearly showed that accumulation of As and Pb were controlled primarily by the anthropogenic factors smelting (A3) and mining (A5), whereas Cd, Cr and Hg accumulation were controlled by the natural factors pH (N5) and watershed (N8). These finding are consistent with the descriptive statistics in Table 1. The high percent exceedance (62%) coupled with a high CV value (2.5) for Pb (Table 1) strongly suggest that anthropogenic factors played a major role in Pb accumulation. In addition, the largest range value of 54 km for Cd and 26 km for Cr, indicate that both showed strong spatial dependence and received comparatively less influence by human activities than the other three trace elements in the study area. The high percent exceedance for Hg (Table 1) can be explained by the local mineral exploitation activity and mechanical transport of watersheds. As Fig. 6 illustrates, the watershed/lithology (N8*N9) interaction had the greatest influence on Hg accumulation over the entire study area. Since elemental Hg is a volatile substance and relatively soluble in water, it can be transported long distances by air and water. In this karst study area, heavy rainfall and high groundwater velocities in carbonates further contribute to Hg migration.

Because the mechanisms of trace element accumulation in karst soils is quite complex and varies around the world, limitations of the present study must be considered when applying our approach and findings to other areas. Background values for trace elements in soil vary tremendously around the world (for geological and climatic reasons), as do specific values for Si (maximum allowable concentration) for trace elements imposed by regulators (for administrative reasons). The specific factors chosen for this investigation may not be universally applicable to all karst areas. The scale of the study area and the specific selection of boundaries can dramatically change the findings vis-à-vis
Fig. 7. The interactive effects of anthropogenic factors land use (A1) and smelting industry (A3) when paired with the other 13 factors on the accumulation of 3 trace elements at different scales. The uppermost bar of each chart is the $q$ value of A1 or A3, and the bars underneath are the interactive $q$ values of A1 or A3 paired the other 13 factors.
identifying the dominant factors influencing trace element accumulation in soils, which is apparent even in this study if one compares the results in Fig. 5 for the entire study area with results for each individual county. Finally, karst areas and karst soils are relatively unique, and the factors considered in this study were selected with that in mind.

5. Conclusions

Anthropogenic factors nonlinearly enhanced the effects of natural factors on the accumulation of 5 trace elements (As, Cd, Cr, Hg, and Pb) in the karst soils. Land use and smelting industry were the anthropogenic factors and watershed was the natural factor with the strongest enhancing effect interacting with other factors. The land use-watershed interaction accounted for 19% of the measured Cd accumulation and the calculated comprehensive pollution risk. The smelting industry-watershed interaction accounted for 19% of the measured As accumulation. Construction had highest pollution risk of the land uses. The findings of this study can be used to develop effective and practical measures to reduce trace element accumulation and pollution risk in karst soils caused by anthropogenic factors, including: (1) reducing pollutant discharges and releases from industrial and mining operations, (2) modifying land use and reducing pollutant discharge from the smelting industry.

CRediT authorship contribution statement

Huan Tao: Writing - original draft, Writing - review & editing, Validation. Xiaoyong Liao: Conceptualization, Project administration, Supervision. You Li: Visualization, Investigation. Chongdong Xu: Methodology, Software, Writing - review & editing. Ganghui Zhu: Data curation, Validation. Daniel P. Cassidy: Writing - review & editing, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was supported in part by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA23010000; XDA19040302) and the Key Research Program of the Chinese Academy of Sciences (KFZD-SW-111).

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