Heavy Metal Pollution Assessment in the Sediment of Rao River, China using the Geo-accumulation Vector

Bao Qian[1,*], Zhe Wang[2] and Feng Yan[3]
[1]*Bureau of Hydrology, Changjiang Water Resources Commission, CWRC, Wuhan 430010, China*
[2]*Hydrology Bureau of Haihe River Water Conservancy Commission, the Ministry of Water Resources, Tianjin 300170, China*
[3]*School of Civil Engineering and Architecture, Nanchang University, Nanchang 330031, China*

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Abstract: The heavy metal plays an significant role in the sediment pollution of the river. However, for the heterogeneity of mineral composition, the background values of elements in sediment often contains uncertainties, which is hard to be treated by the conventional geo-accumulation index. In the present work, the geo-accumulation vector is introduced to deal with the uncertainty of background value and evaluate the pollution of heavy metal in the sediment of Rao River, China. The results show that: the order of pollution degree is: source < upper reaches < estuary < lower reaches < middle reaches. Dexing City, Poyang City and Jingdezhen City are the most polluted area along Rao River, which respectively belong to “moderately to heavily contaminated”, “moderately to heavily contaminated”, and “moderately contaminated” grades, and respectively have risk probabilities of 28%, 8% and 40% to deteriorate. The mean values of the elements in global shale should not be used as the background values of Rao River. Otherwise, the evaluation results of Cu and Cd may be overoptimistic. Compared with the conventional method, the geo-accumulation vector has apparent advantages in dealing with the uncertainty of background values and the recognizing the cross-grade risk.

1 INTRODUCTION

Heavy metal is among the most common river pollutants that are teratogenic and hard to degrade (Xu et al., 2018; Peng et al., 2014). Heavy metal adsorbs onto sediment particles, and its density is greater than that of liquid (Peng et al., 2014; Yan et al., 2018). Thus, the heavy metal load in water environment is easily to be deposited into sediment (Peng et al., 2014; Yan et al., 2018). When the physicochemical environment in water–soil interface is changed, heavy metal could be released into water environment and result in secondary pollution (Yan et al., 2018; Yan et al., 2019a; Yuan et al., 2015). In addition, heavy metal can also be absorbed by submerged macrophyte and benthos and then injure human health by enrichment in food chain (Yan et al., 2018; Yan et al., 2019b; Yuan et al., 2015). To sum up, the heavy metal pollution assessment in the sediment is among the constant research endeavors in river water environment protection.

To assess the pollution of heavy metal in the sediment, Muller (1969) put forward geo-accumulation index model, which determined the pollution degree of heavy metal quantization by synthesizing measured and background value information (Shi et al., 2009). Geo-accumulation index is widely used globally to evaluate heavy metal sediment. For example, Pathak et al. (2013) used the geo-accumulation index to study the metal content of surface sediment of an industrial area adjoining Delhi, India. Zhang et al. applied geo-accumulation index to qualify the heavy metal pollution in ediments of Yangtze River (Zhang et al., 2009). Additionally, Men et al. (2018) used geo-accumulation index to assess the pollution of heavy metal in Beijing, China.

The conventional geo-accumulation index considers the background value of the heavy metal to be definite and unique, and often used the mean value of the element in global shale as the background information (Matschullat et al., 2000; Snežana et al., 2017). However, recent study suggests that this hypothesis does not seem to be reasonable.

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Matschullat showed that the inhomogeneity of sediment mineral distribution results in great deference between local area heavy metal background and whole global element averages (Matschullat et al., 2000). Furthermore, Snežana found that background investigation, such as core acquisition or statistical distribution selection, is always random (Snežana et al., 2017). This behavior leads to a degree of uncertainty in the heavy metals background value, which may significantly affect the application of geo-accumulation index.

Based on statistics principle, Yan et al. improved proposed geo-accumulation vector model to solve the background value uncertainty (Yan et al., 2019a). Heavy metal background is no longer treated as a fixed value but as a random variable in geo-accumulation vector (Yan et al., 2019c). Accordingly, evaluation result is not a unique value, but the probability of pollution status belongs to each level. Geo-accumulation vector was preliminary applied on heavy metal sediment evaluation in West Dongting, which had apparent advantages in rank evaluation and risk factor identification.

The Rao River flows through the Dexing Copper Mine, which is the biggest copper mine in Asia (Ma et al., 2015). Rao River is one of the most heavy-metal polluted rivers in China (Zhang et al., 1995). However, the background value uncertainty greatly affected the results of heavy metal pollution evaluation in Rao River. The objectives of this study are: (i) assessing the pollution status of heavy metal in the sediment of Rao River based on the geo-accumulation vector model; (ii) identifying the risk factor and pollution source of each segment of Rao River; and (iii) further discussing the differences between geo-accumulation index and geo-accumulation vector in environmental assessment.

2 MATERIALS AND METHODS

2.1 Study Area and Methods of Chemical Analysis

As shown in Figure 1, Rao River is located in central China. With an annual runoff of 10.7 billion m^3, Rao River covers a drainage area of 14,367 kilometers (Ma et al., 2015; Zhang, 1995). Rao River has two sources, the northern and southern of which are Chang River and Le'an River, respectively. Rao River flows into Poyang Lake, the largest freshwater lake of China.

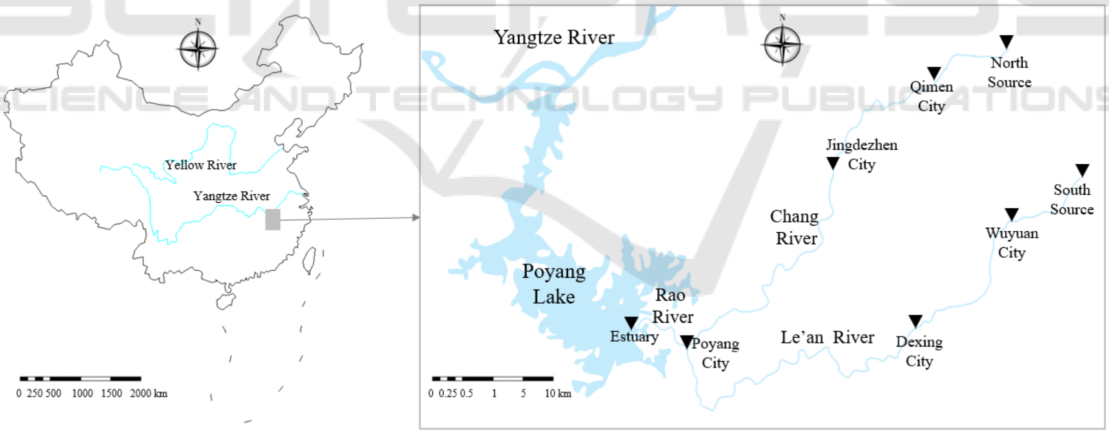

Figure 1: Location of the study area (Filled reverse triangles represent the sampling point).

The land types and economic structure of the cities along the Rao River are quite different. In the upper reaches of Rao River, which majorly contains Qimen City and Wuyuan City, the mountainous proportion exceeds 85%. As a result, the prime economic structure is tourism. The middle reaches of Rao River lies in the mountain-to-plain transitional zone, which contains abundant mineral resources. The prime economic types are therefore industry and mining. For example, Jingdezhen City is famous for its ceramic industry in the world; and Dexing City has the largest opencast copper mine in Asia. The lower reaches Rao River lies in the Poyang City, the land type of which is plain, and the prime economic type is agriculture.

According to Yan et al., the main pollutants in the Rao river basin are copper (Cu), lead (Pb), and cadmium (Cd) (Yan et al., 2018). Therefore, these three indexes are selected for evaluation in this study. To accurately reflect the heavy metal pollution of the river, eight sampling sites were set up in Rao River, as illustrated in Figure 1. Because of the inhomogeneous geological condition of the sediment in Rao River, the geochemical backgrounds of the heavy metals are uncertain intervals instead of concrete values. According to Zhang., the geochemical background of Cu, Pb, and Cd are 14.16 mg/kg-41.97 mg/kg, 13.36 mg/kg-29.38mg/kg, and 0.065 mg/kg-0.257 mg/kg, respectively (Zhang et al., 1995).

The sampling, pretreating, digesting, and measuring methods refer to the Chinese Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (Ministry of Ecological and Environment of the People's Republic of China, 2018). On 14 December 2019, three parallel samples were collected from each site, which were conserved in clean polyethylene bags and sent to the Bureau of Hydrology, Changjiang Water Resources Commission for further analysis. The sediment was first screened through a 1 mm sieve and then naturally air dried. The samples were ground in an agate mortar (SP-40, Shanghai Shupei Corporation, China) and then homogenized and sieved through a 100 µm mesh. After that, 0.5 g samples were digested in a microwave oven (CEM MARS, PyNN Corporation, USA) with an acid mixture (9 mL of 14.0 M HNO_3, 3 mL of 11.7 M HCl, 2 mL of 23.0 M HF, and 2.5 mL of 8.8 H_2O_2). The samples were then condensed to 1–2 mL for total metal analysis.

There were two experimental instrument to make environmental monitoring: the graphite furnace atomic absorption spectrophotometry (ICE3500, Thermofisher Corporation, USA), and the flame atomic absorption spectrophotometry (SK-2003, Persee Corporation, China). Compared with the flame atomic absorption spectrophotometry, the graphite furnace atomic absorption spectrophotometry had a higher sensitivity, but a lower repeatability. As a result, the graphite furnace atomic absorption spectrophotometry was used to use to measure Cd, the concentration of which was relatively lower; while the flame atomic absorption spectrophotometry was used to use to measure Cu and Pb, the concentration of which were relatively higher.

The GSS-7 reference material from the Chinese Environmental Monitoring Center was used to ensure quality, where "GSS-7" was the number of the red soil area in South China. The parallel errors were controlled within 10%, and their average value of three parallel samples was selected as the concentration data to be evaluated.

2.2 Geo-accumulation Index

If M heavy metals are provided to participate in the evaluation, the background and measured values of the mth are b_m and c_m, respectively. Then the geo-accumulation index of the mth heavy metals is calculated as follows:

$$I_m = \log_2 \frac{c_m}{1.5 \cdot b_m} \tag{1}$$

According to the value of I_m, the pollution status of heavy metal m can be classified into the following categories: uncontaminated ($I_m \leq 0$), uncontaminated to moderately contaminated ($0 < I_m \leq 1$), moderately contaminated ($1 < I_m \leq 2$), moderately to heavily contaminated ($2 < I_m \leq 3$), heavily contaminated ($3 < I_m \leq 4$), heavily to extremely contaminated ($4 < I_m \leq 5$) and extremely contaminated ($I_m > 5$) (Ke et al., 2017; Maanan et al., 2017).

In existing literature, the following methods are used to select background values: (i) using the mean value of the element in global shale as the background information and (ii) using geochemistry investigation of the deep core in the evaluation area as the background information (Matschullat et al., 2000; Snežana et al., 2017).

Although the background values determined by method (i) are unique, certain differences in background values exist between the global scale and the evaluation area locally because of the inhomogeneity of the continental geological structure with the mineral composition (Matschullat et al., 2000; Snežana et al., 2017). The results obtained from the method (ii) can approximately reflect the original status of heavy metals in the region. However, because of the randomness of core sampling and the selection of statistical distribution, the background values of heavy metals in sediment are generally not exact values but uncertain interval $b_m \in [l_m, s_m]$ (Snežana et al., 2017). In addition, the traditional geo-accumulation index experiences difficulty dealing with the problem of heavy metal pollution evaluation due to the uncertainty of background values.

2.3 Geo-accumulation Vector

In contrast to the traditional geo-accumulation index model, the ground accumulation vector model uses vector $\boldsymbol{P_m}=\{p_{1m},p_{2m},\ldots,p_{7m}\}$ to reflect the pollution condition, where p_{jm} is the probability of the pollution of the *m*th heavy metal belongs to grade *j* (Yan et al., 2019b).

The universal calculation method can be derived as follows (Yan et al., 2019c):

For grade 1:

$$p_{1m} = p(\log_2 \frac{c_m}{1.5 \cdot b_m} \le 0) = p(b_m \ge \frac{c_m}{1.5}) = \int_{b_m=\frac{c_m}{1.5}}^{+\infty} f(b_m)db_m \tag{2}$$

for *j* =2,3... 6:

$$p_{jm} = p(j-2 < \log_2 \frac{c_m}{1.5 \cdot b_m} \le j-1) = p\left(\frac{c_m}{3 \cdot 2^{j-2}} \le b_m < \frac{c_m}{3 \cdot 2^{j-3}}\right) = \int_{b_m=\frac{c_m}{3 \cdot 2^{j-2}}}^{\frac{c_m}{3 \cdot 2^{j-3}}} f(b_m)db_m \tag{3}$$

and for grade 7:

$$p_{7m} = p(\log_2 \frac{c_m}{1.5 \cdot b_m} > 5) = p(\frac{c_m}{1.5 \cdot b_m} > 2^5) = p(b_m < \frac{c_m}{48}) = \int_{b_m=0}^{c_m/48} f(b_m)db_m \tag{4}$$

In Eq. (2) to Eq. (4), $f(b_m)$ is the probability density function of b_m, which can be generally calculated according to the statistical characteristics of the measured values of the core elements (Yan et al., 2019b). When investigation information is not enough to determine the approximate distribution of b_m, Yan et al. proved that the uniform distribution $U(l_m, s_m)$ is the most likely distribution of $f(b_m)$ at this time based on the maximum entropy principle (Yan et al., 2019b).

In this case, the calculation method of p_{jm} is as follows:

For grade 1:

$$p_{1m} = \begin{cases} 0 & s_m < \dfrac{c_m}{1.5} \\ \dfrac{s_m - (2 \cdot c_m)/3}{s_m - l_m} & l_m \le \dfrac{c_m}{1.5} \le s_m \\ 1 & \dfrac{c_m}{1.5} < l_m \end{cases} \tag{5}$$

for *j* =2,3... 6:

$$p_{jm} = \begin{cases} 1 & \dfrac{c_m \cdot 2^{2-j}}{3} \le l_m < s_m \le \dfrac{c_m \cdot 2^{3-j}}{3} \\ \dfrac{s_m - \left(c_m \cdot 2^{2-j}\right)/3}{s_m - l_m} & l_m < \dfrac{c_m \cdot 2^{2-j}}{3} < s_m < \dfrac{c_m \cdot 2^{3-j}}{3} \\ \dfrac{\left(c_m \cdot 2^{3-j}\right)/3 - l_m}{s_m - l_m} & \dfrac{c_m \cdot 2^{2-j}}{3} < l_m < \dfrac{c_m \cdot 2^{3-j}}{3} < s_m \\ \dfrac{\left(c_m \cdot 2^{3-j}\right)/3 - \left(c_m \cdot 2^{2-j}\right)/3}{s_m - l_m} & l_m < \dfrac{c_m \cdot 2^{2-j}}{3} < \dfrac{c_m \cdot 2^{3-j}}{3} < s_m \\ 0 & s_m \le \dfrac{c_m \cdot 2^{2-j}}{3} \text{ Or } l_m \ge \dfrac{c_m \cdot 2^{3-j}}{3} \end{cases} \tag{6}$$

and grade 7:

$$p_{7m} = \begin{cases} 0 & l_m > \dfrac{c_m}{48} \\ \dfrac{c_m / 48 - l_m}{s_m - l_m} & l_m < \dfrac{c_m}{48} \le s_m \\ 1 & s_m < \dfrac{c_m}{48} \end{cases} \tag{7}$$

Using first-order moment principle for grade recognition, the pollution feature value of $\boldsymbol{P_m}$ is defined as follows:

$$E_m = \sum_{j=1}^{7} p_{jm} \cdot (j-1.5) \tag{8}$$

When Eq. (9) is established, $\boldsymbol{P_m}$ belongs to grade *k*:

$$k-2 < E_m \le k-1 \cdot \tag{9}$$

The risk degree r_m is defined as follows:

$$r_m = \sum_{j=k+1}^{7} p_{jm} \, . \tag{10}$$

Apparently, r_m quantifies the probability that $\boldsymbol{P_m}$ belongs to the grates worse than grade *k* considering the uncertainties in background values.

As mentioned previously, the geo-accumulation vector $\boldsymbol{P_m}=\{p_{1m},p_{2m},\ldots,p_{7m}\}$ reflects the probability that the pollution status of the *m*th heavy metal belongs to each grade (Yan et al., 2019b). To quantify the comprehensive contamination status of heavy metals in the study area, Yan et al. further constructed a comprehensive geo-accumulation vector $\boldsymbol{Q}=\{q_1,q_2,\ldots,q_7\}$, where q_j reflects the probability that the comprehensive contamination of heavy metals in sediments belongs to grade *j* (Yan et al., 2019a). The formula is calculated as follows:

$$q_j = \sum_{m=1}^{M} \left(w_j \cdot p_{jm} \right) \quad j = 1, 2, ..., 7 , \qquad (11)$$

where w_m is the weight of the mth heavy metal.

The grade recognition method of $\boldsymbol{Q}$ is similar to that of $\boldsymbol{P_m}$. The coefficient p_{jm} in Eq. (8) is just replaced with q_j.

Geo-accumulation vector is not a denial to geo-accumulation index. It expands and deepens the traditional geo-accumulation index to uncertainty analysis essentially. Furthermore, to make the discussion more intuitive, p_{jm}, r_m, and q_j can also be represented in forms of percentages (Yan et al., 2019b).

3 RESULT AND DISCUSSION

3.1 Concentrations of Pollutants

The concentrations of the pollutants in the sediment are illustrated in Figure 2.

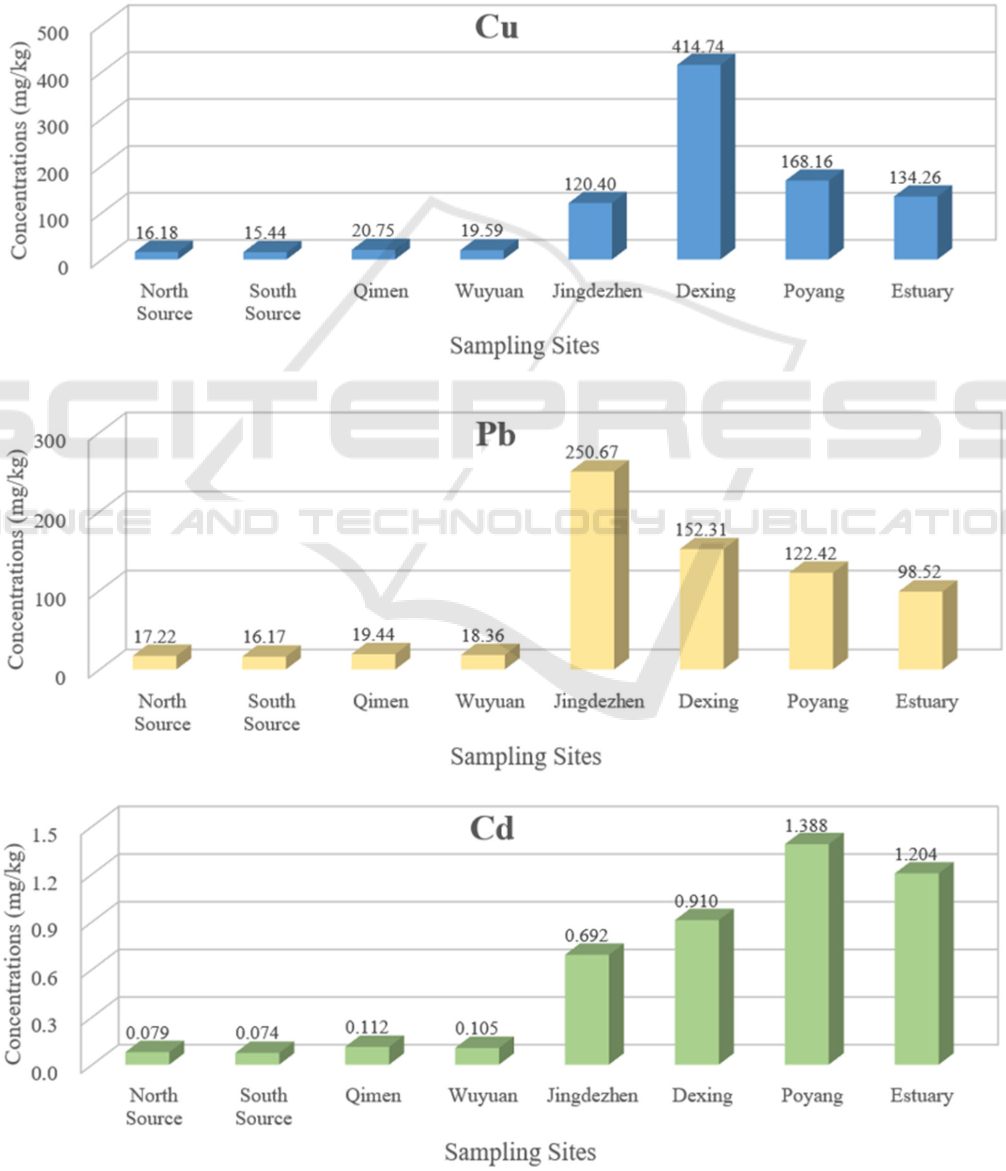

Figure 2: Concentrations of the heavy metals in the sediment along Rao River.

As is shown in Figure 2, the general trends of the contents of Cu and Zn are as follows: source < upper reaches< estuary< lower reaches< middle reaches. Contrary, the general trend of the content of Cd increases as following: source <upper reaches <middle reaches<estuary<lower reaches. The reason for this phenomenon is the difference in the distribution of pollution sources. According to the research of Yan et al, the pollution loads of Cu and Zn majorly come from the industrial activity and mining in Dexing City and Jingdezhen City, which lie along the middle reaches of Rao River; while the pollution loads of Cd majorly comes from the leaching from the red soil of the farmland in the lower reaches of Rao River (Yan et al., 2018).

The mean contents of Cu, Pb and Cd in source region are 15.81mg/kg, 16.70mg/kg and 0.077mg/kg, respectively. Such behavior is close to the lower limit of background values of heavy metals in the sediments of Rao River's water system.

The mean contents of Cu, Pb and Cd in upper reaches region are 20.17 mg/kg, 18.90 mg/kg and 0.109 mg/kg, respectively. Among which, the heavy metals contents in the sediments of Qimen City is about 5% higher than that in Wuyuan City. In comparison with source region, the heavy metals contents of the sediments upper reaches increasingly appear in different degrees. The increase range of Pb and Cu is approximately 20%, whereas that of Cd is over 40%.

The difference of heavy metals contents in middle reaches is so large that the contents of Cu in Dexing City reach up to 414.74 mg/kg, which is around 3.5 times that of Jingdezhen City. The Pb content in Jingdezhen City is 250.67 mg/kg, which is 1.6 times that of Dexing City. Generally, the contents of Cu, Pb and Cd in the middle reaches are about 13, 10 and 7 times of that in the upper reaches and are far beyond the upper limit of background value in Rao River.

The contents of Cu, Pb and Cd in the sediments of lower reaches are 168.16 mg/kg,122.4 2mg/kg, and 1.388 mg/kg, respectively. In contrast to the middle reaches, the contents of Cu and Pb in the lower reaches decline by about 40%, whereas the content of Cd increases by about 60%. In addition, the contents of Cu, Pb and Cd in estuary region are 134.26 mg/kg, 98.52 mg/kg and 1.204 mg/kg, respectively. In comparison with lower reaches, the contents of heavy metals in sediments of estuary region decreases by about 20%.

3.2 The Geo-accumulation Vectors of Pollutants

According to Section 2.3, the geo-accumulation vectors of pollutants are calculated and summarized in Table 1.

Table 1: Summary of calculated geo-accumulation vectors of pollutants.

Sampling Sites	Geo-accumulation Vector	Feature value	Grade	Risk degree
Cu				
North Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
South Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
Qimen	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
Wuyuan	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
Jingdezhen	{0.00,0.37,0.57,0.06,0.00,0.00,0.00}	1.19	moderately contaminated	0.06
Dexing	{0.00,0.00,0.00,0.27,0.62,0.11,0.00}	3.34	heavily contaminated	0.11
Poyang	{0.00,0.00,0.51,0.49,0.00,0.00,0.00}	1.99	moderately contaminated	0.49
Estuary	{0.00,0.00,0.70,0.30,0.00,0.00,0.00}	1.80	moderately contaminated	0.30
Pb				
North Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
South Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
Qimen	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
Wuyuan	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00

Sampling Sites	Geo-accumulation Vector	Feature value	Grade	Risk degree
Jingdezhen	{0.00,0.00,0.00,0.53,0.47,0.00,0.00}	2.97	moderately to heavily contaminated	0.47
Dexing	{0.00,0.00,0.25,0.75,0.00,0.00,0.00}	2.25	moderately to heavily contaminated	0.00
Poyang	{0.00,0.00,0.56,0.44,0.00,0.00,0.00}	1.94	moderately contaminated	0.44
Estuary	{0.00,0.00,0.81,0.19,0.00,0.00,0.00}	1.69	moderately contaminated	0.19
Cd				
North Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
South Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
Qimen	{0.96,0.04,0.00,0.00,0.00,0.00,0.00}	-0.46	uncontaminated	0.04
Wuyuan	{0.96,0.04,0.00,0.00,0.00,0.00,0.00}	-0.46	uncontaminated	0.04
Jingdezhen	{0.00,0.14,0.60,0.26,0.00,0.00,0.00}	1.62	moderately contaminated	0.26
Dexing	{0.00,0.00,0.46,0.54,0.00,0.00,0.00}	2.04	moderately to heavily contaminated	0.00
Poyang	{0.00,0.00,0.14,0.60,0.26,0.00,0.00}	2.62	moderately to heavily contaminated	0.26
Estuary	{0.00,0.00,0.30,0.52,0.18,0.00,0.00}	2.38	moderately to heavily contaminated	0.18

As shown in the Table 1, in the source region, all the metals certainly belong to the "uncontaminated" grade. In the upper reaches, Cu and Pb are still certainly belong to "uncontaminated". Although Cd is also classified "uncontaminated," a 4% risk of being in the "uncontaminated to moderately contaminated" grade exists.

At two sampling cities in the middle reaches, the distinction among each heavy metals' geo-accumulation vectors is substantial. In Jingdezhen City, the pollution sequence is Pb>Cd>Cu. Pb belongs to the "moderately to heavily contaminated" level, and a 47% risk of worsening toward "heavily contaminated" is present. Cu and Cd are classified "moderately contaminated," and the probability of being classified "moderately to heavily contaminated" is 6% and 26%, respectively. In Dexing City, the pollution sequence is Cu>Cd>Pb. Cu belongs to the "heavily contaminated" level, and a 11% risk of worsening toward "heavily to extremely contaminated" exists. Pb and Cd are classified as "moderately to heavily contaminated", and the probabilities of being classified "heavily contaminated" are 44% and 19%, respectively.

In the lower reaches and estuary regions, the sorting of the pollution is Cd>Cu>Pb. The Cd of these two regions belongs to the "moderately to heavily contaminated" level, and the risks of being classified "heavily contaminated" are 26% and 18%, respectively. Likewise, Cu belongs to the "moderately contaminated" level, and the probability of being classified "moderately to heavily contaminated" are 49% and 30%, respectively. Similarly, Pb also belongs to "moderately contaminated" grade, and 44% and 19% chances of worsening to "moderately to heavily contaminated", respectively.

3.3 Comprehensive Geo-Accumulation Vectors Results

Based on the entropy weighting model, the weighted vector {0.39, 0.30, 0.31} is generated for {Cu, Pb, Cd} (Yan et al., 2019c; Yi et al., 2018). Then, according to the Eq. (11), the comprehensive geo-accumulation vectors are calculated and summarized in Table 2.

Table 2: Summary of calculated comprehensive geo-accumulation vectors.

Sampling Sites	Geo-accumulation Vector	Feature value	Grade	Risk degree
North Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
South Source	{1.00,0.00,0.00,0.00,0.00,0.00,0.00}	-0.50	uncontaminated	0.00
Qimen	{0.99,0.01,0.00,0.00,0.00,0.00,0.00}	-0.49	uncontaminated	0.01

Wuyuan	{0.99,0.01,0.00,0.00,0.00,0.00,0.00}	-0.49	uncontaminated	0.01
Jingdezhen	{0.00,0.19,0.41,0.26,0.14,0.00,0.00}	1.85	moderately contaminated	0.40
Dexing	{0.00,0.00,0.22,0.50,0.24,0.04,0.00}	2.60	moderately to heavily contaminated	0.28
Poyang	{0.00,0.00,0.41,0.51,0.08,0.00,0.00}	2.17	moderately to heavily contaminated	0.08
Estuary	{0.00,0.00,0.60,0.34,0.06,0.00,0.00}	1.96	moderately contaminated	0.40

As shown in Table 2, the order of heavy metals pollution in Rao River's sediment is: source < upper reaches < estuary < lower reaches < middle reaches. The source region certainly belongs to "uncontaminated." Although the upper reaches region is also classified "uncontaminated," a 1% risk of worsening to "uncontaminated to moderately contaminated" exists.

In the middle reaches, the pollution level of sediment in Dexing City is "moderately to heavily contaminated," and the risk of worsening toward worse level is 28%. Similarly, the pollution level of sediment in Jingdezhen City is "moderately contaminated," and a 40% risk of worsening to a terrible grade exists. Combined with the discussion in Section 3.2, Cu and Pb cause the deterioration of heavy metals pollution of sediment in Dexing City and Jingdezhen City, respectively.

In the lower reaches and estuary region, the pollution level of heavy metals in sediment is "moderately to heavily contaminated" and "moderately contaminated," respectively. The risks of worsening are 8% and 40%, respectively. Combined with the discussion of Section 3.2, the risk of deterioration is mainly due to Cd.

As mentioned in Section 2.1, it is easily to find that the economic structure and land use type become the major influencing factors of heavy metals pollution in Rao River.

The source and upper reaches regions of Rao River located in the mountainous areas with high forest coverage, where the economic structure is dominated by the less polluting tourism industry. It is therefore suggested that the pollution levels are pretty low in source and upper reaches areas belonging to "uncontaminated."

According to the research of Yan et al, the industrial structure of the middle reaches in Rao River is dominated by industrial activity and mining, whose pollution load is great (Yan et al., 2018). Thus, the pollution condition of heavy metals in sediment of middle reaches is the most serious. Dexing Copper Mine is the largest open copper mine, and Cu in slag is easily leached by rain, which can confluence into the river network with the slope. As a consequence, the main risk factor of sediment in Dexing City is Cu. The industrial structure of Jingdezhen is dominated by ceramic production. Because of the Pb element in the paint of ceramics, the Pb load in industrial wastewater is quite prominent. Based on these findings, the main controlling factor of sediment in Jingdezhen City would be Pb.

The lower reaches of Rao River are located in a plain area, and the soil is mainly red soil with weak acidity, which is conducive to the release of Cd. Besides, the crops in the lower reaches region of Rao River are Indica Rice, which can absorb cadmium well. Farmers are used to returning stalks to their fields after harvest. As rice stalks rot, Cd can easily enter the river network along with farmland runoff. Hence, the main controlling factor in the lower reaches of Rao River seems to be Cd.

3.4 Comparison between Geo-accumulation Index and Geo-accumulation Vector

The mean values of the Cu, Pb and Cd in global shale are 45 mg/kg, 20 mg/kg and 0.3 mg/kg, respectively (Matschullat et al., 2000; Snežana et al., 2017). According to the Eq. (1), the geo-accumulation indices are calculated and summarized in Table 3.

Table 3: Summary of calculated geo-accumulation indices of Rao River.

Sampling Sites	**Geo-accumulation index**	**Grade**
Cu		
North Source	-2.06	uncontaminated
South Source	-2.13	uncontaminated
Qimen	-1.70	uncontaminated

Wuyuan	-1.78	uncontaminated
Jingdezhen	0.83	uncontaminated to moderately contaminated
Dexing	2.62	moderately to heavily contaminated
Poyang	1.32	moderately contaminated
Estuary	0.99	uncontaminated to moderately contaminated
Pb		
North Source	-0.80	uncontaminated
South Source	-0.89	uncontaminated
Qimen	-0.63	uncontaminated
Wuyuan	-0.71	uncontaminated
Jingdezhen	3.06	heavily contaminated
Dexing	2.34	moderately to heavily contaminated
Poyang	2.03	moderately to heavily contaminated
Estuary	1.72	moderately contaminated
Cd		
North Source	-2.51	uncontaminated
South Source	-2.60	uncontaminated
Qimen	-2.01	uncontaminated
Wuyuan	-2.10	uncontaminated
Jingdezhen	0.62	uncontaminated to moderately contaminated
Dexing	1.02	moderately contaminated
Poyang	1.63	moderately contaminated
Estuary	1.42	moderately contaminated

Compared between Table 2 and Table 3, it is easily to find that there are two differences between the geo-accumulation index and geo-accumulation vector.

(i) In the evaluation of Cu and Cd, the evaluation results of the geo-accumulation index are looser than the geo-accumulation vector.

In the middle reaches, lower reaches and estuary region, the pollution grades of Cu and Cd in Table 3 are about one category lower than those in Table 1. The reason for this phenomenon is that the local background values is not identified with their mean values in global shale. For example, the background values of Cu and Cd in the sediment of Rao River are 14.16 mg/kg-41.97 mg/kg, and 0.065 mg/kg-0.257 mg/kg, respectively. While their mean values in global shale are 45 mg/kg and 0.3 mg/kg. Obviously, compared with global shale, the natural content of Cu in the sediment of Rao River is much lower. As the result, using the global average value as the local background may lead to the distortion that some anthropogenic heavy metals are regarded as the natural background, which makes the evaluation overoptimistic.

(ii) Compared with the geo-accumulation vector, it is hard for the geo-accumulation index to identify risks.

As shown in Table 3, the geo-accumulation index of Cu in the estuary region is 0.99, which is nearly to the “moderately contaminated” grade. However, the geo-accumulation index cannot recognize this cross-grade risk, rather would be considered that it certainly seems to be “uncontaminated to moderately contaminated”.

By contrary, the geo-accumulation vector solves this problem through introducing the risk degree. For example, as indicated in Table 1, the pollution feature value of Cu in Poyang City is 1.99, which belongs to the “moderately contaminated” grade. Considering its risk degree is 0.49, we can further deduce that the pollution of Cu in Poyang City has a potential possibility of 49% to worsen to the "moderately to heavily contaminated" grade.

4 CONCLUSIONS

In the sediment of Rao River, the pollution degrees of heavy metals have significant regional differences, and the main causes for these differences are the economic structure and land use type. The order of pollution degree is: source < upper reaches < estuary < lower reaches < middle reaches. Dexing City, Poyang City and Jingdezhen City are the most polluted area along Rao River, which belong to "moderately to heavily contaminated", "moderately to heavily contaminated" and "moderately contaminated" grades, respectively, and have risk probabilities of 28%, 8% and 40% to deteriorate, respectively. The critical controlling heavy metals of these 3 cities are Cu, Pb and Cd, respectively. The fundamental causes would be their ceramic industry, copper mining, and the red soil.

For the heterogeneity of mineral composition, the mean values of the elements in global shale should not be used as the background values of Rao River. Otherwise, the evaluation results of Cu and Cd may be overoptimistic.

Compared with the conventional geo-accumulation index, the geo-accumulation vector has apparent advantages in dealing with the uncertainty of background values and the recognizing the cross-grade risk.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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