

The Application of Numerical Characteristics to the Distribution Characteristics of Copper in the Liao River, China

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Abstract

The aim of the present investigation was to research the distribution characteristics of copper in water and sediment of the Liao River, China. The concentrations of copper in water and sediment showed significant difference at different sampling stations. The distribution characteristics of copper in water and sediment were obtained by using discrete and continuous numerical characteristics. The results indicated that the average concentrations of copper in water and sediment decreased slightly after its accumulation. While the deviations of the concentrations of copper in water and sediment from the expectation increased significantly after its accumulation. The skewness distributions of the concentrations of copper in water and sediment did not change much before and after its accumulation. The kurtosis distributions of the concentrations of copper in water and sediment decreased significantly after its accumulation. Therefore, the precise distribution characteristics of copper in water and sediment were obtained through the combination of the discrete and continuous numerical characteristics.

Keywords

Discrete Type, Continuous Type, Numerical Characteristics, Pollution Assessment

1. Introduction

Copper is one of the most toxic heavy metals in ecosystems [1] [2]. In addition, excessive copper concentration may endanger organisms and humans through food chains [3] [4]. According to the Annual Research and Consultation Report

of Panorama Survey and Investment Strategy on China Industry (2013-2017) and Chinese Dietary Reference Intakes (2016), the critical concentration of copper was 0.002 mg/L for fish and the tolerable upper intake level of copper was 8 mg per day for adult [5].

The Liao River has a total length of 1430 km and drainage area of 229,000 km². The Liao River runs through Hebei, Neimenggu and Jilin Province and flows into Bohai Bay near Panjin City in Liaoning Province (Figure 1). According to the Environmental Quality Standards for Surface Water of China (GB 3838-2002) and Environmental Quality Standard for Soils of China (GB 15618-2008), water and sediment of river systems had been seriously polluted by heavy metals and other pollutants [6] [7]. Therefore, it is necessary to investigate the distribution and accumulation characteristics of heavy metal in water and sediment of the Liao River for preventing heavy metal hazards.

Expectation, standard deviation, skewness and kurtosis are numerical characteristics of random variable and have important theoretical and practical significance. Borah *et al.* investigated heavy metal contamination of groundwater with respect to cadmium, manganese, zinc and copper in India by using univariate

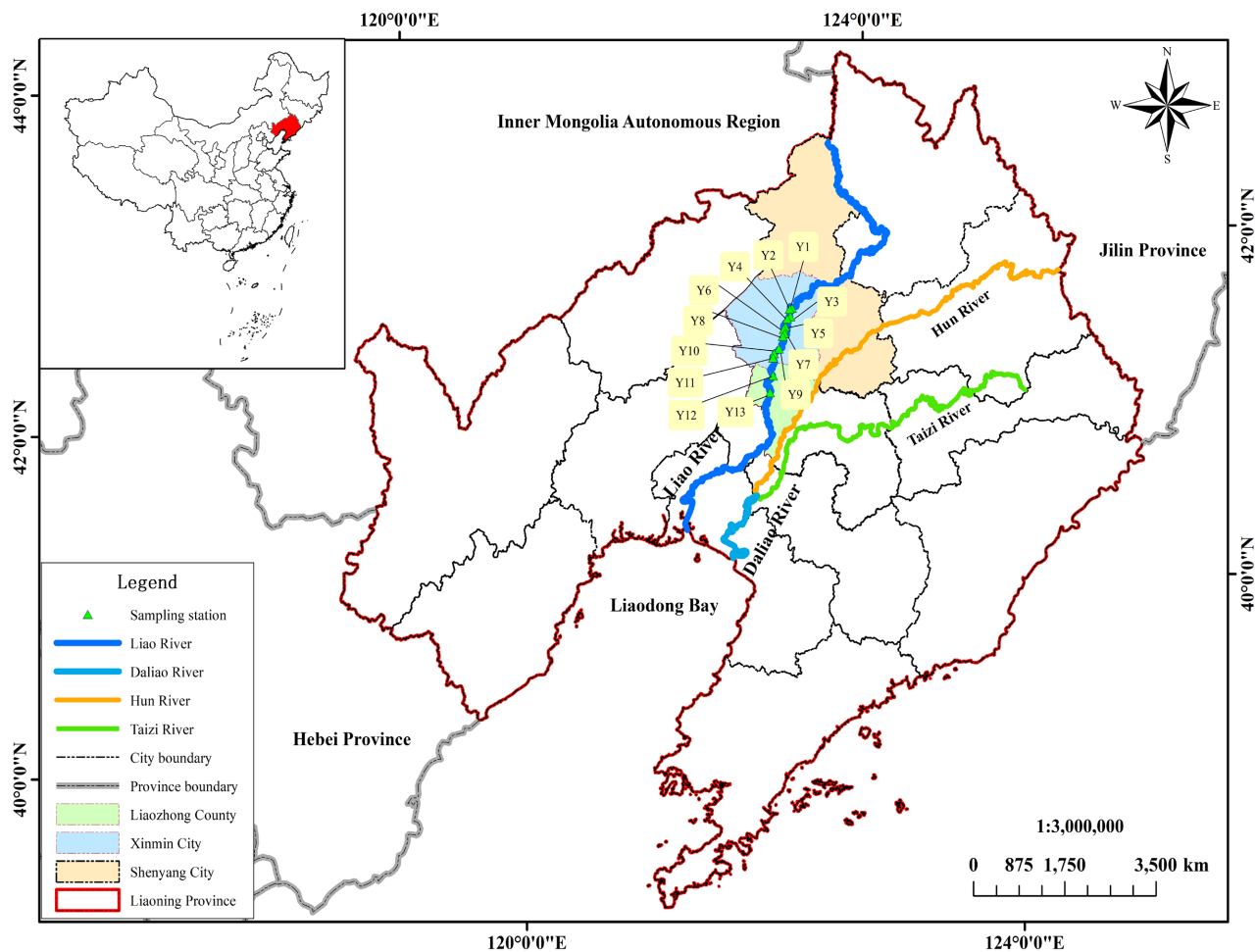


Figure 1. The Liao river basin.

statistics, skewness and kurtosis [8]. Feng *et al.* investigated the distribution characteristics of dissolved arsenic in water of the Pu River by using three types of expectation and standard deviation calculations [9]. Liu *et al.* studied the compositions and particle size distributions of surface sediment and the distributions characteristics of Cd, Cr, Cu, Ni, Pb, and Zn in sediment of the Tai Lake by using discrete expectation, skewness and kurtosis [10]. Xie *et al.* explored the optimization of arsenic monitoring points in cultivated land of Jiangmen City in Guangdong Province by using discrete expectation, standard deviation and sandwich sampling method [11]. However, it is difficult to obtain the accurate distribution and accumulation characteristics of heavy metal only by using expectation and standard deviation. For example, the same expectation and standard deviation may have different distribution and fluctuation characteristics. Of course, skewness and kurtosis theory partially optimize expectation and standard deviation theory. In addition, the continuous numerical characteristics can effectively obtain the distribution and accumulation characteristics of heavy metal after its accumulation. In this paper, we obtained the distribution and accumulation characteristics of copper in water and sediment of the Liao River by combining discrete and continuous numerical characteristics. The accurate distribution and accumulation characteristics of copper provided a theoretical basis for the prevention and control of copper pollution in water and sediment of the Liao River.

2. Materials and Methods

The geographic coordinates of the research area are $41^{\circ}35'47''\text{N}$ - $42^{\circ}3'40''\text{N}$, $122^{\circ}41'11''\text{E}$ - $122^{\circ}59'35''\text{E}$. The research area traverses Shenyang city and provides irrigating water for agricultural production. The research area has a total length of 89 km. We transform the spatial coordinate $0 \text{ km} \leq x \leq 89 \text{ km}$ into unit interval $0 \text{ km} \leq x \leq 1 \text{ km}$ for simplifying the calculation [9]. According to the morphology and hydrology of the Liao River, thirteen water and sediment sampling stations were chosen to investigate the concentrations of copper in water and sediment of the Liao River on 23 June, 2018 (Figure 1).

The research area crosses both industrial and agricultural areas of Shenyang city. Therefore, the research area is clearly representative for studying the impact of industry and agriculture on heavy metal pollution in water and sediment of the Liao River. Three water and sediment samples were respectively selected at each sampling station. Water samples were collected from the Liao River at a depth of approximately 5 - 10 cm below surface water using polyethylene acid-washed containers [9]. Sediment samples were collected from the Liao River at a depth of approximately 3 - 5 cm below surface sediment and then stored in polyethylene containers [12]. The concentrations of copper in water and sediment samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS). The analytical procedures were subjected to strict quality control measures. The statistical analysis was done by Matlab.

3. Results

3.1. The Concentrations of Copper in Water and Sediment of the Liao River

According to the Environmental Quality Standards for Surface Water (GB 3838-2002) and Soil Environmental Quality (GB 15618-2018), the critical concentrations of copper in water and sediment are 10 $\mu\text{g/L}$ and 50 mg/kg , respectively. The concentrations of copper in water and sediment were 20.620 to 49.317 $\mu\text{g/L}$ and 4.115 to 9.871 mg/kg , respectively (**Table 1**). The highest concentration of copper in water appeared at Y13, which was attributed to livestock and poultry industry and transportation industry near Y13 [13] [14]. The highest concentration of copper in sediment appeared at Y5, which was attributed to high concentration of copper in water and geographical features near Y5 [15] [16]. According to variance analysis, the concentrations of copper in water and sediment showed significant difference at different sampling stations ($P = 0.000 < 0.01$). Therefore, we have to adopt different measures to control copper pollution in water and sediment at different sampling stations. For example, reducing copper pollution caused by livestock and poultry industry and transportation industry is a priority task for controlling copper pollution in water near Y13 [17] [18] [19]. However, reducing high concentration of copper in water and the cumulative effect of copper is a priority task for controlling copper pollution in sediment near Y5 [20] [21].

Table 1. The concentrations of copper in water and sediment.

Code	The concentrations of copper in water ($\mu\text{g/L}$)	The concentrations of copper in sediment (mg/kg)
Y1	33.830 \pm 1.149	5.587 \pm 0.457
Y2	27.233 \pm 1.009	8.424 \pm 0.453
Y3	41.797 \pm 1.049	8.492 \pm 0.518
Y4	45.627 \pm 1.001	8.383 \pm 0.407
Y5	48.213 \pm 1.002	9.871 \pm 0.354
Y6	38.157 \pm 1.050	7.989 \pm 0.501
Y7	31.833 \pm 1.011	6.184 \pm 0.607
Y8	33.713 \pm 1.007	7.757 \pm 0.638
Y9	32.210 \pm 0.547	8.349 \pm 0.751
Y10	20.620 \pm 1.000	4.115 \pm 0.345
Y11	47.463 \pm 1.008	6.502 \pm 0.392
Y12	23.677 \pm 0.844	4.244 \pm 0.453
Y13	49.317 \pm 1.510	7.525 \pm 0.866

Each value represents the mean \pm SE.

3.2. The Distribution Characteristics of Copper in Sediment

3.2.1. The Discrete Distribution Characteristics of Copper in Sediment

Let C_i denote the concentration of copper in sediment at the i th sampling station and ξ represent the random variable of the concentration of copper. According to **Table 1**, the discrete expectation and standard deviation of copper in sediment were respectively obtained by

$$E\xi = \frac{1}{13} \sum_{i=1}^{13} C_i = 7.186 \text{ mg/kg} \quad (1)$$

and

$$S\xi = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (C_i - E\xi)^2} = \sqrt{\frac{1}{12} \sum_{i=1}^{13} (C_i - 7.186)^2} = 1.742 \text{ mg/kg}. \quad (2)$$

Formula (2) indicated that the fluctuation characteristics of the concentrations of copper in sediment were not intense, which might be due to relative stability of copper ion in sediment [22] [23]. However, the concentrations of copper in sediment from Y2 to Y6, Y8, Y9 and Y13 were higher than discrete expectation. Field research showed that industry, agriculture, livestock and poultry industry and transportation industry contributed a lot of copper to sediment [24] [25]. While the concentrations of copper in sediment at Y1, Y7, Y10, Y11 and Y12 were far less than the discrete expectation. Therefore, the discrete expectation and standard deviation are unable to describe accurate distribution characteristics of copper in sediment. Skewness is a measure of asymmetry of a data set in statistics. However, kurtosis describes the peakedness or tailedness of the distribution of a set of data. By Formula (1) and **Table 1**, the discrete skewness and kurtosis of copper in sediment were respectively obtained by

$$Skew(\xi) = \frac{\frac{1}{n} \sum_{i=1}^n (C_i - E\xi)^3}{\left[\frac{1}{n} \sum_{i=1}^n (C_i - E\xi)^2 \right]^{3/2}} = \frac{\frac{1}{13} \sum_{i=1}^{13} (C_i - 7.186)^3}{\left[\frac{1}{13} \sum_{i=1}^{13} (C_i - 7.186)^2 \right]^{3/2}} = -0.530 \quad (3)$$

and

$$Kurt(\xi) = \frac{\frac{1}{n} \sum_{i=1}^n (C_i - E\xi)^4}{\left[\frac{1}{n} \sum_{i=1}^n (C_i - E\xi)^2 \right]^2} = \frac{\frac{1}{13} \sum_{i=1}^{13} (C_i - 7.186)^4}{\left[\frac{1}{13} \sum_{i=1}^{13} (C_i - 7.186)^2 \right]^2} = 2.285. \quad (4)$$

Formula (3) and skewness theory theoretically explained that the concentrations of copper in sediment at most sampling stations were higher than discrete expectation. Formula (4) and kurtosis theory indicated that the concentration curve of copper in sediment was not steep, which verified the slight copper pollution in sediment. It is clear that the skewness and kurtosis theory effectively overcome the shortcomings of the expectation and standard deviation theory. However, the discrete numerical characteristics are difficult to obtain the distribution characteristics of copper in sediment after its accumulation.

3.2.2. The Continuous Distribution Characteristics of Copper in Sediment

By using curve fitting toolbox and **Table 1**, the concentration function $\psi(x)$ of copper in sediment was defined by

$$\begin{aligned} \psi(x) = & 5.596 - 1.504x + 6.688x^2 - 3.067x^4 + 14.28x^7 \\ & + 12.7x^2 \sin(-2.051x^4) + 3.242x^2 \cos(22.11x^3) \end{aligned} \quad (5)$$

where $0 \leq x \leq 1$ was the spatial coordinate of sampling station, $R^2 = 0.9093$.

By average formula and Formula (5), the continuous expectation and standard deviation of copper in sediment were respectively defined by

$$E\xi = \int_0^1 [\psi(x)] dx = 5.580 \text{ mg/kg} \quad (6)$$

and

$$S\xi = \sqrt{\int_0^1 (x - 5.580)^2 \psi(x) dx} = 12.031 \text{ mg/kg}. \quad (7)$$

By Formulas (1) and (6), the continuous expectation was less than discrete expectation. That was to say, the average concentration of copper in sediment decreased slightly after its accumulation. However, Formulas (2) and (7) indicated that the continuous standard deviation was far greater than discrete standard deviation. Therefore, Formula (2), Formula (7), **Table 1** and **Table 2** theoretically explained that the concentration of copper in sediment at Y1 increased significantly after its accumulation. Therefore, the cumulative effect of copper pollution may cause serious harm to organisms and humans through food chains

Table 2. The absolute error between $\psi(x)$, $\theta(x)$ and the measured data.

Code	$\psi(x)$ (mg/kg)	The absolute error between $\psi(x)$ and the measured data (mg/kg)	$\theta(x)$ ($\mu\text{g/L}$)	The absolute error between $\theta(x)$ and the measured data ($\mu\text{g/L}$)
Y1	5.596	0.009	28.470	5.360
Y2	5.539	2.885	35.583	8.349
Y3	5.618	2.874	41.490	0.306
Y4	5.811	2.572	45.122	0.504
Y5	6.017	3.854	44.770	3.443
Y6	5.917	2.072	38.335	0.178
Y7	5.277	0.907	31.362	0.472
Y8	5.600	2.157	36.357	2.644
Y9	6.960	1.389	31.278	0.932
Y10	3.033	1.082	20.714	0.094
Y11	6.317	0.185	47.010	0.454
Y12	4.177	0.067	23.968	0.291
Y13	7.510	0.015	49.409	0.092

[26] [27] [28]. However, the continuous expectation and standard deviation also have their own shortcomings. For example, the continuous expectation and standard deviation are unable to obtain the complete distribution and accumulation characteristics of copper in sediment.

By Formulas (5), (6) and (7), the continuous skewness and kurtosis of copper in sediment were respectively defined by

$$Skew(\xi) = \frac{E(x - E\xi)^3}{[S(\xi)]^3} = \frac{\int_0^1 [(x - 5.580)^3 \psi(x)] dx}{12.031^3} = -0.425 \quad (8)$$

and

$$Kurt(\xi) = \frac{E(x - E\xi)^4}{[S(\xi)]^4} = \frac{\int_0^1 [(x - 5.580)^4 \psi(x)] dx}{12.031^4} = 0.182. \quad (9)$$

Formula (8) and skewness theory explained that the concentrations of copper in sediment at most sampling stations were higher than continuous expectation. For example, the concentrations of copper in sediment at Y1, Y3, Y4, Y5, Y6, Y8, Y9, Y11 and Y13 all exceeded continuous expectation. The serious copper pollution areas in sediment revealed by continuous numerical characteristics were slightly different from those by discrete numerical characteristics. For example, the discrete numerical characteristics indicated that the serious copper pollution area in sediment was from Y2 to Y6. However, the continuous numerical characteristics indicated that the serious copper pollution area in sediment was from Y3 to Y6. This might be caused by some interfering factors such as soil type, geographical structure and copper ions released from sediment into water near Y2 [29] [30]. Formulas (4) and (9) indicated that the continuous kurtosis was far less than discrete kurtosis of copper in sediment. The above results theoretically verified that the concentrations of copper in sediment tended to be stable after its accumulation. Therefore, the continuous numerical characteristics partially overcome the shortcomings of discrete numerical characteristics and obtain the distribution and accumulation characteristics of copper in sediment after its accumulation. However, the continuous numerical characteristics also have their own shortcomings. For example, the continuous numerical characteristics are difficult to consider the differences and specific characteristics of copper pollution at different sampling stations.

3.3. The Distribution Characteristics of Copper in Water

3.3.1. The Discrete Distribution Characteristics of Copper in Water

Let W_i denote the concentration of copper in water at the i th sampling station and η represent the random variable of the concentrations of copper. According to **Table 1**, the discrete expectation and standard deviation of copper in water were respectively obtained by

$$E\eta = \frac{1}{13} \sum_{i=1}^{13} W_i = 36.438 \mu\text{g/L} \quad (10)$$

and

$$S\eta = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (W_i - E\eta)^2} = \sqrt{\frac{1}{12} \sum_{i=1}^{13} (W_i - 36.438)^2} = 9.545 \mu\text{g/L}. \quad (11)$$

Formulas (2) and (11) indicated that the fluctuation characteristics of the concentrations of copper in water were far greater than those in sediment. That was to say, the concentrations of copper in water were more easily affected than those in sediment [31] [32] [33]. By Formula (10) and **Table 1**, the discrete skewness and kurtosis of copper in water were respectively obtained by

$$Skew(\eta) = \frac{\frac{1}{n} \sum_{i=1}^n (W_i - E\eta)^3}{\left[\frac{1}{n} \sum_{i=1}^n (W_i - E\eta)^2 \right]^{3/2}} = \frac{\frac{1}{13} \sum_{i=1}^{13} (W_i - 36.438)^3}{\left[\frac{1}{13} \sum_{i=1}^{13} (W_i - 36.438)^2 \right]^{3/2}} = -0.098 \quad (12)$$

and

$$Kurt(\eta) = \frac{\frac{1}{n} \sum_{i=1}^n (W_i - E\eta)^4}{\left[\frac{1}{n} \sum_{i=1}^n (W_i - E\eta)^2 \right]^2} = \frac{\frac{1}{13} \sum_{i=1}^{13} (W_i - 36.438)^4}{\left[\frac{1}{13} \sum_{i=1}^{13} (W_i - 36.438)^2 \right]^2} = 1.813. \quad (13)$$

Formula (12) indicated that discrete skewness of copper in water was basically close to zero. Formula (12) and skewness theory theoretically explained that the concentrations of copper in water at about half of sampling stations exceeded discrete expectation, which was basically consistent with the measured data. Formulas (11), (12) and **Table 1** also indicated that the concentrations of copper in water were almost symmetrical distribution centered on discrete expectation. Formula (13) and kurtosis theory also explained the fluctuation characteristics of the concentrations of copper in water after its accumulation.

3.3.2. The Continuous Distribution Characteristics of Copper in Water

By using curve fitting toolbox and **Table 1**, the concentration function $\theta(x)$ of copper in water was obtained by

$$\theta(x) = 28.47 + 87.93x - 384.8x^3 + 565.4x^5 - 280.1x^7 - 59.79x^3 \sin(15.68x^4) + 115.2x^4 \cos(17.58x^2) \quad (14)$$

where $0 \leq x \leq 1$ was the spatial coordinate of sampling station, $R^2 = 0.8911$.

The continuous expectation, standard deviation, skewness and kurtosis of copper in water were respectively defined by

$$E\eta = \int_0^1 [\theta(x)] dx = 30.470 \mu\text{g/L}, \quad (15)$$

$$S(\eta) = \sqrt{\int_0^1 [x - E(\eta)]^2 \theta(x) dx} = 166.045 \mu\text{g/L}, \quad (16)$$

$$Skew(\eta) = \frac{E(x - E\eta)^3}{[S(\eta)]^3} = \frac{\int_0^1 (x - 30.470)^3 [\theta(x)] dx}{166.045^3} = -0.181 \quad (17)$$

and

$$Kurt(\eta) = \frac{E(x - E\eta)^4}{[S(\eta)]^4} = \frac{\int_0^1 (x - 30.470)^4 [\theta(x)] dx}{166.045^4} = 0.033. \quad (18)$$

Formulas (10) and (15) indicated that the continuous expectation was far less than discrete expectation of copper in water. That was to say, the concentrations of copper in water showed a significant decrease trend after its accumulation. This might be attributed to the transport of some copper ions in water to downstream, sediment and aquatic organisms in various ways [34] [35]. Formulas (2), (7), (11) and (16) also indicated that the concentrations of copper in water were easily affected by many influencing factors after its accumulation. Formulas (12) and (17) indicated that the continuous skewness was far less than discrete skewness of copper in water. Therefore, Formula (17) and skewness theory partially verified that the concentrations of copper in water at Y10 and Y12 were very low. Formulas (13) and (18) indicated that the continuous kurtosis was less than discrete kurtosis of copper in water. However, the concentrations of copper in water at Y10 and Y13 increased significantly after its accumulation. The continuous kurtosis of copper in water seemed to have lost its effect. However, field research showed that livestock and poultry industry and transportation industry caused persistent copper pollution to water near Y10 and Y13.

4. Discussion

Expectation, standard deviation, skewness and kurtosis are numerical characteristics of random variable and have important theoretical and practical significance. However, it is hard to obtain accurate distribution characteristics of copper pollution in water and sediment only considering one or two items of expectation, standard deviation, skewness, and kurtosis. It may obtain comprehensive distribution characteristics of copper pollution in water and sediment by combining expectation, standard deviation, skewness and kurtosis. In addition, continuous and discrete numerical characteristics have their own advantages and disadvantages. For example, discrete numerical characteristics mainly obtain the distribution characteristics of copper pollution in water and sediment at discrete sampling station. However, continuous numerical characteristics mainly obtain the distribution characteristics of copper pollution in water and sediment throughout the whole research area. Of course, discrete and continuous numerical characteristics cannot effectively consider some influencing factors of copper pollution in water and sediment. For example, copper in water of the Liao River may be affected by the existing form of copper, velocity of water flow, temperature, etc. While copper pollution in sediment of the Liao River may be affected by the soil type, organic matter, pH, existing form of copper and the concentration of copper in water, etc. Therefore, it is difficult to obtain true distribution characteristics of copper in water and sediment by only considering numerical characteristics. Therefore, we have to combine numerical characteristics with field research for obtaining the distribution and accumulation characteristics of copper in water and sediment.

5. Conclusion

The discrete and continuous numerical characteristics reveal different distribution characteristics of copper in water and sediment before and after its accumulation, which provide a theoretical basis for adopting different treatment measures of copper pollution in water and sediment. In addition, the combination of discrete and continuous numerical characteristics may provide a new perspective and direction for researching the distribution and accumulation of copper in water and sediment before and after its accumulation. Moreover, the mixed use of multiple numerical characteristics, such as expectation, standard deviation, skewness and kurtosis, can obtain more accurate distribution characteristics. Of course, the distribution characteristics of copper in water and sediment may be affected by some influencing factors. Therefore, how to combine the discrete and continuous numerical characteristics with influencing factors for obtaining accurate distribution and migration regularity of copper in water and sediment is an important research direction of the subsequent research. In addition, more mathematical tools, such as numerical result and figure plot, can be provided to explain the distribution characteristics of heavy metal pollution in water and sediment of the Liao River.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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