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Study on heavy metal concentrations in river sediments through the total amount evaluation method*

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Abstract: A quantitative method to evaluate the amounts of heavy metals in river sediments is established. Using the BT Drainage River in North China as a study object, six representative cross sections were selected for measurement of heavy metal indicators in sediments, and then the main contamination indicators were determined by performing a potential ecological risk assessment. Using a section of this river as an example, the total amounts of the main pollution indicators and those of their harmful forms are estimated by the Surfer software, which simulates the pollution status within the downstream sediments of the outfall at this section. The calculation results could provide a theoretical guideline and data support for pollution treatment of the BT Drainage River.

Key words: Total amount evaluation, Heavy metal pollution, River sediments, Surfer software
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1 Introduction

As an important component of a water environment, river sediment is not only the place where pollutants accumulate from the water body, but also a secondary pollution source which has a potential impact on water quality. Under certain conditions, the pollutants in sediments will be released and result in secondary pollution (Hua *et al.*, 2006). Sediment pollution, especially from heavy metals, has an important impact on water environment and a direct or potential threat on human health and aquatic ecosystems. At present, there are several methods used to dispose of river sediments in China, which include marine dumping, reclamation, landfill, disposing, and utilizing, etc. The premise of selecting an appropriate treatment method is to identify the characteristics of sediment pollution and the amounts of pollution indicators.

In recent years, a large number of studies on heavy metal pollution in sediments were performed, and many ways of assessing heavy metal pollution in sediments were proposed, such as geo-accumulation index, enrichment factor, pollution load index, potential ecological index, and hazard quotient (Singh *et al.*, 2003; Burton *et al.*, 2005; Caeiro *et al.*, 2005; Visuthismajarn *et al.*, 2005; Chen *et al.*, 2007; Rodriguez-Barroso *et al.*, 2009). The geo-accumulation index and potential ecological index are widely applied now.

In this paper, using the BT Drainage River as the research object, firstly heavy metal indicators in sediments of the river are measured, and the main

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pollution indicators are determined using the potential ecological index. Then the Surfer software is employed to simulate spatial distribution of two kinds of major heavy metals and evaluate their total amounts so as to provide data support and decision basis for the next engineering control of the river pollution.

2 Materials and methods

2.1 Sample collection and monitoring results

According to geomorphic features, the status of main sewage outfalls, and principles for selecting sediment monitoring points, six sections where the main outfalls situate are selected as sediment sampling points and labeled as I, II, III, IV, V, and VI in sequence (Fig. 1). Surface sediment samples of 60-cm thickness are collected and divided into upper, middle, and lower layers, with a 20-cm thickness for each layer. The sediment samples are collected four times, respectively, in August 2007, October 2007, March 2008, and May 2008. Heavy metal indicators of these sediment samples are measured, which are Cu, Zn, Cd, Cr, and Pb. The monitoring results are shown in Table 1.

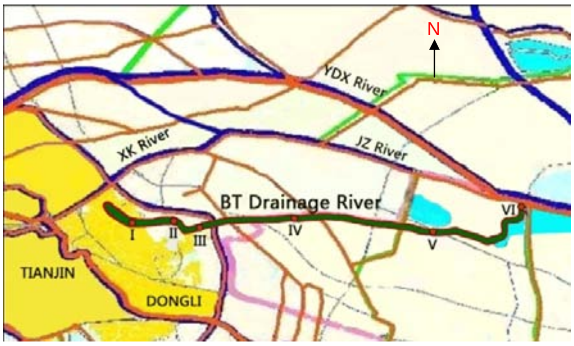

Fig. 1 Sketch map of monitoring sections of the BT Drainage River, China

2.2 Determination of main pollution indicators in sediments of the BT Drainage River

The potential ecological risk index is employed to calculate potential ecological risk factors of heavy metals so as to assess their pollution status in each layer of the sediments in the six sections. According to Hakanson (1980) and Kucuksezgin *et al.* (2008), the model to calculate the potential ecological risk factors of heavy metals is

Table 1 Heavy metal concentrations in sediments of the BT Drainage River

Section	Sediment	Concentration (mg/kg (dry sediment))				
		Cu	Zn	Cd	Cr	Pb
I	Upper	1231.77	1620.52	9.68	430.61	103.33
	Middle	334.00	704.11	7.18	290.00	138.82
	Lower	87.70	423.57	2.95	163.24	51.88
II	Upper	630.22	411.01	6.80	219.34	47.65
	Middle	272.44	425.27	4.06	85.87	49.78
	Lower	26.71	164.20	1.78	84.05	40.90
III	Upper	1904.12	1501.10	6.94	338.39	60.23
	Middle	197.90	277.17	5.27	85.22	29.52
	Lower	59.41	341.68	1.22	94.73	18.93
IV	Upper	1224.96	2731.12	8.38	350.18	70.89
	Middle	621.01	1111.54	8.47	344.94	73.80
	Lower	314.28	527.65	5.46	158.27	58.87
V	Upper	2006.67	1144.77	5.68	236.58	78.57
	Middle	384.83	495.54	4.47	208.72	49.04
	Lower	302.12	516.45	4.57	173.02	65.76
VI	Upper	308.61	534.65	7.57	118.10	84.81
	Middle	216.70	654.62	6.89	96.63	40.94
	Lower	94.37	211.69	6.40	175.45	86.65

$$E_{\mathrm{f}}^{i} = T_{\mathrm{f}}^{i} \cdot C_{\mathrm{f}}^{i}, \tag{1}$$

where C_{f}^{i} is the contamination factor of a heavy metal, and can be calculated by $C_{\mathrm{f}}^{i} = C^{i} / C_{\mathrm{n}}^{i}$, where C^{i} is the measured concentration of the heavy metal in dry sediment, and C_{n}^{i} is the standard pre-industrial reference level. The toxic coefficients are standardized as T_{f}^{i}, according to the toxic levels of heavy metals. The values of C_{n}^{i} and T_{f}^{i} for Cu, Zn, Cd, Cr, and Pb are shown in Table 2 (Hakanson, 1980). The total potential ecological risk index for several heavy metals can be expressed by $\mathrm{RI} = \sum E_{\mathrm{f}}^{i}$. The potential ecological risk of heavy metals is classified into five levels according to the values of E_{f}^{i} and RI (Table 3).

Firstly C_{f}^{i} of the five heavy metals are calculated in the terms of C_{n}^{i} in Table 2 and C^{i} in Table 1. Then according to C_{f}^{i} and T_{f}^{i} in Table 2, E_{f}^{i} of the heavy metals and RI for each section are calculated in terms of Eq. (1) (Table 4).

Table 2 Values of C_n^i and T_f^i for Cu, Zn, Cd, Cr, and Pb

Element	C_n^i (mg/kg)	T_f^i	Element	C_n^i (mg/kg)	T_f^i
Cu	50	5	Cr	90	2
Zn	175	1	Pb	70	5
Cd	1.0	30			

Table 3 Classification of potential ecological risk according to E_f^i and RI

E_f^i	RI	Potential ecological risk
<20	<75	Low
20–40	75–150	Moderate
40–80	150–300	Considerable
80–160	>300	High
>160		Very high

Table 4 Assessment data of heavy metals in river sediments at each section

Section	Sediment	E_f^i					RI
		Cu	Zn	Cd	Cr	Pb	
I	Upper	123.20	9.26	290.40	9.56	7.40	439.82
	Middle	33.40	4.02	215.40	6.44	9.90	269.16
	Lower	8.75	2.42	88.50	3.62	3.70	106.99
II	Upper	63.00	2.35	204.00	4.88	3.40	277.63
	Middle	27.25	2.43	121.80	1.90	3.55	156.93
	Lower	2.65	0.94	53.40	1.86	2.90	61.75
III	Upper	190.4	8.58	208.20	7.52	4.30	419.00
	Middle	19.80	1.58	158.10	1.90	2.10	183.48
	Lower	5.95	1.95	36.60	2.10	1.35	47.95
IV	Upper	122.50	15.61	251.40	7.78	5.05	402.34
	Middle	62.10	6.35	254.10	7.66	5.25	335.46
	Lower	31.45	3.02	163.80	3.52	4.20	205.99
V	Upper	200.65	6.54	170.40	5.26	5.60	388.45
	Middle	38.50	2.83	134.10	4.64	3.50	183.57
	Lower	30.20	2.95	137.10	3.84	4.70	178.79
VI	Upper	30.85	3.06	227.10	2.62	6.05	269.68
	Middle	21.65	3.74	206.70	2.14	2.90	237.13
	Lower	9.45	1.21	192.00	3.90	6.20	212.76
Mean value		56.76	4.38	172.95	4.51	4.56	243.16

As shown in Table 4, according to the RI value for each layer of the sections, heavy metal contamination in the upper layer is more serious than those in the lower one for each section, principally due to the fact that the upper layer is closer to the water body. Contaminations in the upper layer of Sections I, III, IV, and V and in the middle layer of Section IV reach a high degree of potential ecological risk, and most of the others show considerable levels. According to E_f^i for each heavy metal, in general, contaminations of Cu and Cd reach considerable and very high degrees of potential ecological risk while the others have low potential ecological risks. The contamination of Cd shows the highest values in all layers of each section except for the upper layer of Section V where the contamination of Cu shows the highest value. Instead, Cu only focuses in upper layer but shows much lower values in the middle and lower layers. It indicates that considerable Cu contamination sources probably emerge recently. Therefore, Cu and Cd are determined as the main pollution indicators in sediments of the BT Drainage River to be analyzed selectively.

2.3 Surfer software and calculation principle

In recent years, the Surfer software is the most widespread interpolation and graphics software, and has the capability of mapping and data processing. It provides three models to calculate volume, which are based on the expanded Ladder Rule, expanded Simpson's Rule, and expanded Simpson 3/8 Rule. In this study, the expanded Simpson 3/8 Rule is adopted to calculate the volumes of digital elevation model (DEM), expressed by (Han and Meng, 2007):

$$A_i = \frac{3\Delta x}{8}(G_{i,1} + 3G_{i,2} + 3G_{i,3} + 2G_{i,4} + \cdots + 2G_{i,n-1} + G_{i,n}), \tag{2}$$

$$V \approx \frac{3\Delta y}{8}(A_1 + 3A_2 + 3A_3 + 2A_4 + \cdots + 2A_{n-1} + A_n), \tag{3}$$

where A_i and V are the volumes of the ith grid cell and the whole grid region, respectively; Δx and Δy are the column distance along x axis and the row distance along y axis of a mesh DEM, respectively; $G_{i,j}$ is the node elevation.

Using Section III as an example, the amounts of main heavy metal pollution indicators in sediments are calculated based on the theories and functions of the Surfer software in the calculation of earthwork (Wang *et al.*, 2006). The concentrations of heavy metals at each sampling point are regarded as the concentrations in the whole profile where the point is included. Thus, the amount of each heavy metal in sediments can be calculated by

$$G = \sum_{j=1}^{n} (C_j \cdot S_j) \cdot G_{\mathrm{d}} / S_{\mathrm{s}}, \qquad (4)$$

where $\sum_{j=1}^{n} (C_j \cdot S_j)$ can be calculated by the software, C_j and S_j are the concentrations of the heavy metal in the jth grid and the area of the jth grid, respectively, and j and n represent the jth grid and the amount of the grids, respectively; G_{d} is the mass of dry sediments, calculated by $G_{\mathrm{d}}=V\rho(1-\omega)$, where V, ρ, and ω are the volume, density, and water content of sediments, respectively; S_{s} is the area of sediments.

The sediments are divided into the upper, middle, and lower layers, so the total amount of the heavy metal in sediments equals the sum of the contents in the three layers, which can be expressed as

$$G = \sum_{i=1}^{3} \sum_{j=1}^{n} (C_j \cdot S_j)_i \cdot V_i \cdot \rho_i \cdot (1-\omega_i) / S_{\mathrm{s}}, \qquad (5)$$

where i represents the upper, middle, or lower sediment accordingly while its value equals 1, 2, or 3, respectively.

3 Results and analysis

3.1 Total amount evaluation of heavy metals

The sediment samples were collected in September 2008 at the outfall near Section III and 10, 20, 50, 100, 200, and 500 m along the downstream from the outfall for the determination of Cu and Cd. Then the determining result was input into the computer for the evaluation of C_j by the software. Fig. 2 shows the concentration status of Cu in the upper, middle, and lower sediments along the downstream from the outfall, respectively. The highest content of Cu is concentrated in the first 100 m of the upper sediments (Fig. 2a) in contrast of lower sediments (Fig. 2c) which showed the highest Cu concentrations between 200 and 500 m. The content of Cu steadily increases in the 100 to 500 m range in the middle layer (Fig. 2b). These distribution characteristics of Cu are mainly due to the combination of deposition law of heavy metal, natural condition of the river, and varying pollution discharge status of the outfall near Section III.

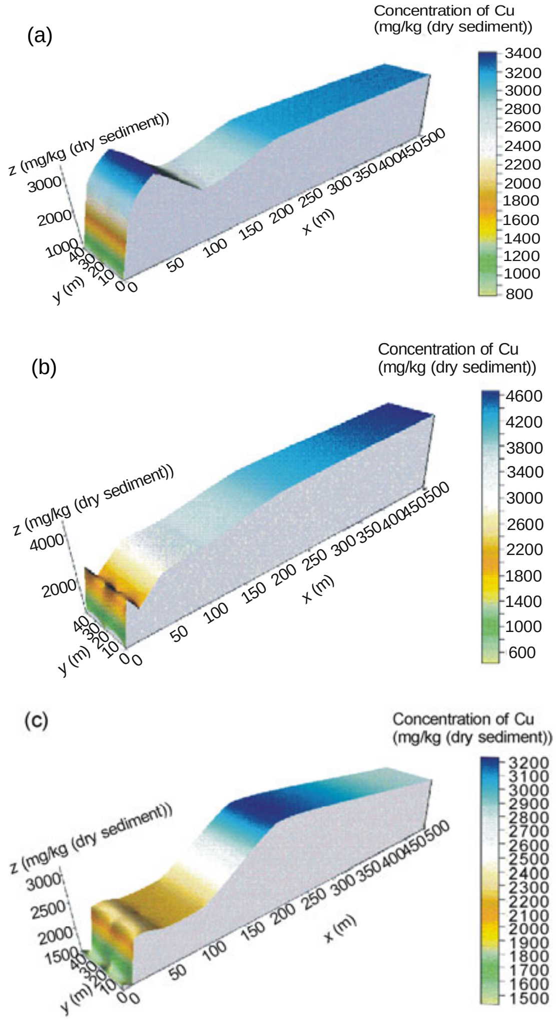

Fig. 2 Contamination simulation of Cu in upper (a), middle (b), and lower (c) sediments
x: distance to the outfall; *y*: width of the river; *z*: concentration of heavy metal

3.2 Total amount evaluation of harmful forms of heavy metals

Ion exchangeable, carbonate, Fe-Mn oxidative, and the organic form of heavy metals are comparatively easy to cause harm to animals and plants, and thus they are considered to be harmful forms of heavy metals. The contamination of total harmful forms of Cu in the upper, middle, and lower sediments is simulated as shown in Fig. 3. The distribution characters of harmful forms amount of Cu in each layer are very similar to its total amount distributions, which are shown in Fig. 2. Thus, there is a reasonable direct proportional relationship between the two values.

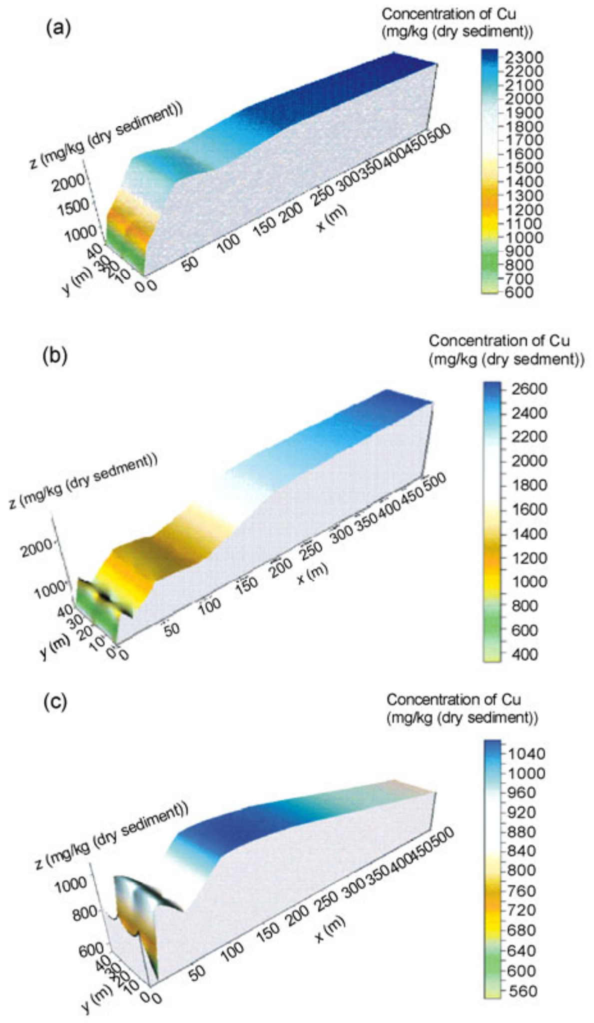

Fig. 3 Contamination simulation of harmful forms of Cu in upper (a), middle (b), and lower (c) sediments
x: distance to the outfall; *y*: width of the river; *z*: concentration of heavy metal

The density and water content in each layer of sediments were measured (Table 5). All the parameters were substituted into Eq. (5) to calculate the total amounts of Cu and Cd and their harmful forms in sediments within the 500 m downstream from the outfall near Section III with the width of 40 m and the depth of 60 cm. Then it concludes that the total amounts of Cu and Cd are 26.65×10^3 and 105.20 kg, respectively, and their total harmful form amounts are 12.31×10^3 and 42.44 kg, respectively, which can be used as a quantitative basis for sediment disposal.

Table 5 Density and water content of each layer sediment

Sediment	Density (g/cm^3)	Water content (%, w/w)
Upper	1.53	81
Middle	1.77	62
Lower	1.90	39

4 Conclusions

Heavy metal contamination status in sediments of the BT Drainage River was assessed through the potential ecological risk index. Most of the sections reached a high degree or a considerable degree of potential ecological risk especially in upper layers. Cu and Cd were determined to be the main contamination indicators according to their much higher E_{f}^{i} values than the other heavy metals in all layers of the six sections. Moreover, Cu shows much higher values in upper layer than in middle and lower layers, which indicates that considerable Cu contamination sources probably emerge recently. Using Cu as an example, the Surfer software was applied to simulate the pollution status and evaluate its total amount and total harmful form amount in sediments within the 500 m downstream from the outfall near Section III with the width of 40 m and the depth of 60 cm. The simulation result for each layer presents various distributions, which should due to a series of causes including the deposition law of heavy metal, natural condition of the river, and varying pollution discharge status of the outfall. However, the total amount and total harmful form amount of Cu in each layer presumably show a direct proportional relationship. The evaluating results of Cd were obtained by the same approach. The calculated total amounts of Cu and Cd are 26.65×10^3 and 105.20 kg, respectively, and their total harmful form amounts are 12.31×10^3 and 42.44 kg, respectively. Due to high precision of the Surfer software, the calculated results can provide reliable data support and reference for selection of sediment treatment method allowing for according sediment contamination of the BT Drainage River to be controlled effectively and fundamentally.

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