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Potential toxic risk of heavy metals from sediment of the Pearl River in South China

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Abstract

Based on the monitoring of five heavy metal elements in the surface sediments of the Pearl River in South China, potential toxicity of the heavy metals was assessed using consensus-based sediment quality guidelines (SQGs) method and geo-accumulation (I_{geo}) index method. The monitoring results showed the heavy metal concentrations were significantly and positively correlated with each other, demonstrating a common trend in variation of concentration in the surface sediments. The assessment using the consensus-based SQGs method showed the potential toxicity of Cu was the highest, and Cd was the lowest. The evaluation based on mean probable effect concentration (PEC) quotient showed the region was seriously polluted with high toxicity heavy metals. Correlation analysis revealed a significant and positive correlation between the mean PEC quotient and the average of I_{geo} with a correlation coefficient of 0.926 ($n = 23$, $P < 0.01$). In conclusion, the consensus-based SQGs and mean PEC quotient are applicable to assess potential toxicity risks of heavy metals in freshwater sediments in the Pearl River.

Key words: sediment quality guidelines; sediment; heavy metal; potential toxicity

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Introduction

The sediments at the bottom of the water column play a major role in the pollution scheme of the river systems (Forstner, 1985). Sediments can reflect the quality of water system and can be used to detect insoluble contaminants in water. Their capacity to accumulate contaminants is an important factor to assess environmental impact on aquatic ecosystems (Silva and Rezende, 2002). Depending on hydrodynamics, biogeochemical processes and environmental conditions (redox, pH, salinity and temperature) of rivers, sediments act as an important sink of heavy metals in aquatic systems, as well as a potential non-point source which may directly affect overlying waters (Damian, 1988; Bruces *et al*., 1996; Balls *et al*., 1997; Santos Bermejo *et al*., 2003). Adsorbed heavy metals can be desorbed from sediments and cause a secondary pollution when environmental conditions change (Segura *et al*., 2006). Heavy metals are among the most persistent pollutants due to their resistance to decomposition in natural conditions (Fan *et al*., 2002). Such elements tend to accumulate in the surface sediments, and may affect population health if the contents reach levels at which they constitute toxic pollutants (Marchand *et al*., 2006; Pekey, 2006; Tan *et al*., 2006; Li *et al*., 2006).

Because sediment quality guidelines (SQGs) can predict the potential toxicity of contaminated sediment and identify the aquatic sediment area, numerical SQGs for freshwater ecosystems and marine ecosystems have been developed (Macdonald *et al*., 2000; Fan *et al*., 2006). Some of SQGs have been used successfully to assess sediment pollution in many countries of the world, such as Australia (Mccready *et al*., 2006), and Portugal (Mil-Homens *et al*., 2006). However, there is no report about using SQGs in the assessment of freshwater sediment pollution in China.

The Pearl River is the second largest river in China next to the Yangtze River and is ranked the 13th in terms of discharge volume in the world (Zhao, 1990; Yin *et al*., 2004). The Pearl River system is mainly composed of three tributaries: Xijiang, Beijiang and Dongjiang. Its mean annual discharge volume is about 336 billion m^3. The period of high flow, from April to September, accounts for 80% of the annual discharge volume. Low flow season is from October to March, and the flushing time is about 22 d during this season (Hong *et al*., 2005). The Pearl River stretches for 2214 km and drains an area of 452000 km^2 (Zhao, 1990). It carries a sediment load of 80×10^6 tons/year (Tian, 1994; Zhang *et al*., 1999). The suspended sediment concentration in the Pearl River is lower compared with other major rivers in China with a mean concentration about 0.172 g/L and an annual flux

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30.64×10^6 tons (Wai *et al*., 2004). About 94% of the suspended sediment is discharged during the wet season (April to September), 80% of which is deposited at the Pearl River estuary and the remainder transported to the South China Sea (Wai *et al*., 2004; Hu *et al*., 2006).

Guangzhou, the capital city of Guangdong Province, lies at the top of the Pearl River estuary. The Beijiang River runs through the city. The Guangzhou region (113°0′–114°0′E, 23°0′–23°20′N) of the Pearl River starts from Yagang, runs through Guangzhou City until the new harbor of Huangpu. A massive economic growth and urban development in Guangzhou has led to excessive release of wastewater into the Guangzhou section of the Pearl River (Li *et al*., 2000).

This study uses consensus-based SQGs (Macdonald *et al*., 2000) to evaluate the contaminations of heavy metals in surface sediments of the Pearl River (Guangzhou region), and compare the results with the index of geo-accumulation (I_{geo}). The aim of this article is to show whether the consensus-based SQGs is applicable to assess surface sediments in the Pearl River.

1 Methods

1.1 Sampling design and analytical methods

In this research project, five heavy metals were monitored at 23 cross sections of surface sediments in the Pearl River (Guangzhou region) and main creeks in Guangzhou (Fig. 1). Among which, there were 10 monitoring sections on the main stream: 1 (Yagang), 2 (Yingjinghai), 15 (Zhujiangdaqiao), 6 (Huangsha), 19 (Haizhuqiao), 20 (Zhongdamatou), 8 (Huanandaqiao), 21 (Pazhoudaqiao), 9 (Changzhou) and 10 (Huangpuxingang), and 13 monitoring sections on the main creeks. In order to reflect the degree of sediment pollution, 5 sampling sites were assigned on every monitoring section on the main stream, and 3 sampling sites on the main creeks according to river width. The concentrations of heavy metals sampled at every monitoring section were determined, and the averages over a monitoring section were used to represent a contamination concentration of the region.

Sediment samples were collected in July 2007. Sediment was sampled to a depth of approximately 9 cm using a Ponar Type Grab sampler (602-014, 23 cm × 23 cm Heavyweight Grab Sampler, Rickly Hydrological Company, USA). Samples were placed in a polyethylene bag, then placed in cooler, covered with ice and shipped immediately to Sun Yat-sen University.

Sediment samples were air dried. For metal analysis, samples were digested with the mixture of HNO_3-HNO_4-HF as described by Wei and Qi (1988). Analysis was performed using an Atom Absorption Spectrophotometer (Hitachi Z-5000, Japan). Cu, Pb, Zn and Cr were determined by flame atomic absorption, and Cd was determined

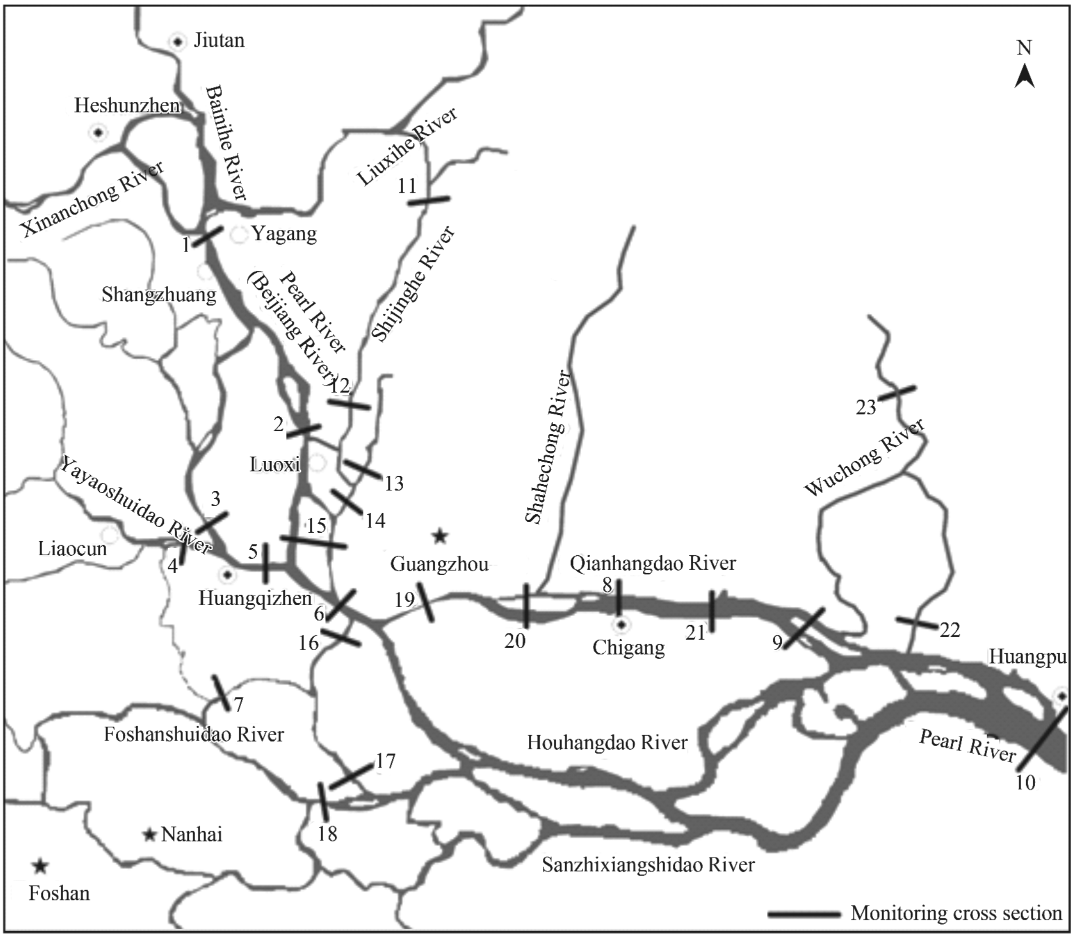

Fig. 1 Distribution of monitoring cross sections.

by graphite furnace atomic absorption spectrometry. The soil standard substance (ESS-3, GSBZ50013-88), issued by the China National Environmental Monitoring Centre, was analyzed along with the samples. Analytical precision was in good agreement. The relative errors for all elements were generally less than 5%.

1.2 Evaluation methods

1.2.1 Sediment quality evaluation method

Consensus-based SQGs (including consensus-based TECs (threshold effect concentrations) and consensus-based PECs (probable effect concentrations)), developed by Macdonald *et al*. (2000), were used to evaluate sediment pollution degree in this study. Macdonald *et al*. (2000) assembled and classified the published SQGs into two categories: a threshold effect concentration (TEC), below which adverse effects are not expected to occur; and a probable effect concentration (PEC) above which adverse effects are expected to occur more often than not. Consensus-based TECs were calculated by determining the geometric mean of the published TEC-type values. Likewise, consensus-based PECs were calculated by determining the geometric mean of the published PEC-type values.

For each sediment sample, mean PEC quotient was the average of the ratio of each contaminant concentration to its corresponding PEC. In this article, the potential toxicity of each monitoring region was expressed as the mean PEC quotient of five heavy metals. In this evaluation, sediment samples were predicted to be not toxic if mean PEC quotients were < 0.5, otherwise if > 0.5, sediment samples were toxic (Macdonald *et al*., 2000).

1.2.2 Index of geo-accumulation

The index of geo-accumulation was first introduced by Müller (1969). $I_{\rm geo}$ is a quantitative index to research heavy metal contamination in aquatic sediment and has been widely used to evaluate the contamination degree of heavy metals in surface sediment. Its calculation formula is as follows (Eq. (1)):

$$I_{\rm geo} = \log_2\left(\frac{C_{sn}}{K\times C_{\mathrm{B}n}}\right) \qquad (1)$$

where, C_{sn} is the measured concentration of the heavy metal n in the sediment; $C_{\mathrm{B}n}$ is the concentration of the heavy metal n in Beijiang River sediment. The $C_{\mathrm{B}n}$ of Cd, Cr, Zn, Cu and Pb is 0.72, 35, 55, 16.4, 36.6 mg/kg respectively (Huang *et al*., 1989). K is the background matrix correction factor which takes account of the variation of the trace metal in the background materials due to lithogenic effects (K = 1.5). $I_{\rm geo}$ provides a classification system for the degree of pollution when compared to the background (Table 1) (Fostner *et al*., 1981).

1.3 Statistical methods

Correlation analyses were carried out using statistical computer software (SPSS11.0).

Table 1 Relationship between $I_{\rm geo}$ and pollution level

$I_{\rm geo}$ value	Class of $I_{\rm geo}$	Pollution level
⩽ 0	0	Unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to strongly polluted
3–4	4	Strongly polluted
4–5	5	Strongly to very strongly polluted
>5	6	Very strongly polluted

2 Results and discussion

2.1 Monitoring results

The monitoring results of five heavy metal elements of this study, the background values (Huang *et al*., 1989) and the average contents of Hong Kong river sediments (Jia *et al*., 1997) are shown in Table 2. The average contents of pollutants in surface sediments of the Pearl River (Guangzhou region) were higher than background values. Especially, the average content of Cu was 21.2 times of the background value. The average contents of Cd, Zn, and Pb in the Pearl River (Guangzhou region) sediments were nearly the same with that in Hong Kong river sediments. But the average contents of Cr and Cu in the Pearl River (Guangzhou region) sediments were higher than that in Hong Kong river sediments obviously, up to 1.9 and 3.1 times, respectively.

The correlation coefficients between heavy metal concentrations are shown in Table 3. The result showed the heavy metals were significantly and positively correlated

Table 2 Contents of heavy metals in the sediments of the Guangzhou section of the Pearl River (mg/kg)

Sampling site	Cd	Cr	Zn	Cu	Pb
1	0.50	6.7	172.6	101.8	61.9
2	1.47	92.3	375.3	290.8	78.6
3	2.13	174.0	462.0	530.5	95.2
4	2.48	116.7	365.6	609.7	91.0
5	2.53	125.8	491.6	588.2	118.4
6	2.70	151.7	472.3	594.3	165.8
7	2.70	162.0	426.6	672.6	162.7
8	1.74	46.6	383.2	274.9	83.7
9	1.15	50.7	324.1	212.6	76.9
10	0.75	10.9	262.7	119.4	64.0
11	1.09	41.8	380.7	117.9	82.6
12	2.17	158.2	343.0	419.9	109.4
13	1.20	147.6	346.7	259.2	52.7
14	1.06	69.8	352.9	301.6	115.7
15	1.39	120.7	433.4	322.9	113.1
16	4.15	215.5	560.7	829.4	219.6
17	2.24	133.9	454.4	437.3	99.4
18	2.18	143.5	411.0	315.2	125.5
19	0.21	8.3	302.5	169.5	91.4
20	2.01	65.3	401.9	242.6	94.5
21	1.80	55.9	375.5	180.6	108.9
22	0.73	27.8	488.4	248.1	104.2
23	1.07	14.7	230.1	165.0	43.8
Average	1.72	93.1	383.4	348.0	102.6
Background value[a]	0.72	35	55	16.4	36.6
Hong Kong river sediment[b]	2.11	48.5	385.4	112.7	114.5

[a] Huang *et al*., 1989; [b] Jia *et al*., 1997.

with each other, demonstrating a common trend of concentration variation in the surface sediments.

2.2 Assessing results of the consensus-based sediment quality guidelines

The values of consensus-based TECs and consensus-based PECs (Macdonald *et al*., 2000) are shown in Table 4. It could be seen that the potential toxicity of Cu was the highest, but that of Cd was the lowest in study area.

The mean PEC quotient of heavy metals can express the potential toxicity to some extent. As shown in Fig. 2, only 3 monitoring sections (including 1, 10 and 23) with mean PEC quotients < 0.5 can be considered as non-toxicity, the other sections all were toxicity. As a whole, the sections were seriously polluted with heavy metals, especially the Shuikoushui Creek, Yayao Creek, Huadi Creek and the trunk stream section after they merged, posing a high toxicity risk. It showed the same trend in variation of concentration with the result obtained by Zheng *et al.* (1996) in 1991–1995.

Table 3 Correlation coefficient matrix between heavy metal concentrations in the sediments of the Guangzhou region of the Pearl River (n = 23)

Element	Cd	Cr	Zn	Cu	Pb
Cd	1				
Cr	0.837**	1			
Zn	0.711**	0.687**	1		
Cu	0.894**	0.849**	0.716**	1	
Pb	0.779**	0.666**	0.742**	0.782**	1

** Significance at $P < 0.01$.

Table 4 TECs and PECs benchmark values for heavy metals in freshwater ecosystem (mg/kg)

Item	Cd	Cr	Zn	Cu	Pb
Consensus-based TEC	0.99	43.4	121	31.6	35.8
Consensus-based PEC	4.98	111	459	149	128

2.3 Assessing results of the index of geo-accumulation

According to the calculation equation of I_{geo} and the monitoring results of five heavy metals, the values of I_{geo} and their classes were calculated (Table 5). The average I_{geo} indicated that the pollution degree of five heavy metals decreased as following sequence: Cu > Zn > Pb > Cr > Cd.

As shown in Table 5, the pollution degree of 5 monitoring cross sections (including 3, 5, 6, 7, 16) reached 3 (moderately to strongly polluted), 4 monitoring cross sections (including 10, 11, 19 and 23) reached 1 (unpolluted to moderately polluted), only section 1 was class 0 (unpolluted), and the rest sections reached 2 (moderately polluted). As a whole, the Shuikoushui Creek, Yayao Creek, Huadi Creek and the trunk stream section after they merged were seriously polluted with heavy metals.

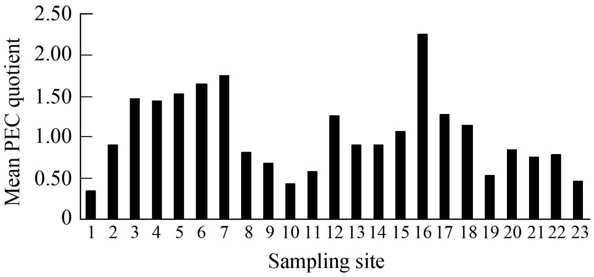

Fig. 2 Estimated mean PEC quotient of surface sediments in the Guangzhou region of the Pearl River.

Table 5 I_{geo} and their class of heavy metals in the sediments of each sampling site

Sampling site	Cd		Cr		Zn		Cu		Pb		Average	
	I_{geo}	Class	I_{geo}	Class	I_{geo}	Class	I_{geo}	Class	I_{geo}	Class	I_{geo}	Class
1	–1.11	0	–2.97	0	1.06	2	2.05	3	0.17	1	–0.16	0
2	0.44	1	0.81	1	2.19	3	3.56	4	0.52	1	1.51	2
3	0.98	1	1.73	2	2.49	3	4.43	5	0.79	1	2.08	3
4	1.20	2	1.15	2	2.15	3	4.63	5	0.73	1	1.97	2
5	1.23	2	1.26	2	2.58	3	4.58	5	1.11	2	2.15	3
6	1.32	2	1.53	2	2.52	3	4.59	5	1.59	2	2.31	3
7	1.32	2	1.63	2	2.37	3	4.77	5	1.57	2	2.33	3
8	0.69	1	–0.17	0	2.22	3	3.48	4	0.61	1	1.36	2
9	0.09	1	-0.05	0	1.97	2	3.11	4	0.49	1	1.12	2
10	–0.53	0	–2.27	0	1.67	2	2.28	3	0.22	1	0.28	1
11	0.01	1	-0.33	0	2.21	3	2.26	3	0.59	1	0.95	1
12	1.01	2	1.59	2	2.06	3	4.09	5	0.99	1	1.95	2
13	0.15	1	1.49	2	2.07	3	3.40	4	–0.06	0	1.41	2
14	–0.03	0	0.41	1	2.10	3	3.62	4	1.08	2	1.43	2
15	0.36	1	1.20	2	2.39	3	3.71	4	1.04	2	1.74	2
16	1.94	2	2.04	3	2.76	3	5.08	6	2.00	2	2.76	3
17	1.05	2	1.35	2	2.46	3	4.15	5	0.86	1	1.97	2
18	1.01	2	1.45	2	2.32	3	3.68	4	1.19	2	1.93	2
19	–2.36	0	–2.66	0	1.87	2	2.78	3	0.74	1	0.07	1
20	0.90	1	0.31	1	2.28	3	3.30	4	0.78	1	1.52	2
21	0.74	1	0.09	1	2.19	3	2.88	3	0.99	1	1.38	2
22	–0.57	0	–0.92	0	2.57	3	3.33	4	0.92	1	1.07	2
23	–0.01	0	–1.84	0	1.48	2	2.75	3	–0.33	0	0.41	1
Average	0.67	1	0.83	1	2.22	3	3.82	4	0.90	1	1.69	2

Class 6: very strongly polluted; 5: strongly to very strongly polluted; 4: strongly polluted; 3: moderately to strongly polluted; 2: moderately polluted; 1: unpolluted to moderately polluted; 0: unpolluted.

What was the reason? On one hand, the section received a large amount of industrial and residential wastewater from Foshan City where was an upriver catchment. On the other hand, the section also received a large amount of wastewater from Guangzhou City, because it lay in the urban center of Guangzhou. This showed that the pollution degree of sediments was closely related with anthropogenic sources. The result was consistent with the many studies of sediment pollution, for example, Perkins *et al*. (2000) found that Pb, Zn, Cr, and Cu concentrations in surficial wetland sediments all increased with increasing proximity to anthropogenic sources.

2.4 Comparison of the two assessing methods

The assessing results of the consensus-based SQGs and that of the index of geo-accumulation were similar, and the main pollutants and polluted sites were almost the same. Correlation analysis revealed a significant and positive correlation between the mean PEC quotient and the average I_{geo} with correlation coefficient 0.926 (n = 23, $P < 0.01$), suggesting that the two methods are rather high in conformity. Therefore, the consensus-based SQGs and mean PEC quotient are applicable to assess potential toxicity risks of heavy metals in the study area.

3 Conclusions

Assessing results of the consensus-based SQGs revealed that in study area the potential toxicity of Cu was the highest, but that of Cd was the lowest. The evaluation based on mean PEC quotient showed that the sections were seriously polluted with heavy metals, especially Shuikoushui Creek, Yayao Creek, Huadi Creek and the trunk stream section. After they merged, a high toxicity risk was posed.

Correlation analysis revealed a significant and positive correlation between the mean PEC quotient and the average I_{geo}. The correlation coefficient is 0.926 (n = 23, $P <$ 0.01). In conclusion, the consensus-based SQGs and mean PEC quotient are applicable for the assessment of potential toxicity risks of heavy metals in freshwater sediments in the Pearl River.

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