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ORIGINAL ARTICLE

Sediment quality assessment for heavy metal pollution in the Xiang-jiang River (China) with the equilibrium partitioning approach

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Abstract Sediment quality criteria (SQC) of heavy metals (copper, lead, zinc and cadmium) for surface sediment have been developed to evaluate sediment contamination in the Xiang-jiang River of China using the equilibrium partitioning approach. USEPAs fresh water quality criteria [criterion continuous concentration (CCC), criterion maximum concentration (CMC)] were referenced to derive sediment quality criteria (SQC-low and SQC-high) of the Xiang-jiang River. The toxicological implications of SQC-low and SQC-high were similar with CCC and CMC, which were used to protect benthic organisms from short-term- and long-term exposure to pollutants. Sediment Pollution Index method was established based on the SQC-low and SQC-high values to evaluate sediment quality qualitatively and quantitatively. The evaluation method was applied to the Xiang-jiang River, and the result indicated that the cadmium contamination in the sediments was of concern; especially, in the Zhu-zhou, Yue-yang, and the middle and downstream reaches of Heng-yang section.

Keywords Equilibrium partitioning approach · Heavy metal · Sediment quality criteria · Sediment quality assessment · The Xiang-jiang River

Introduction

Heavy metal pollutions in sediments have been widely investigated due to their highly toxicity, long-term persistence, and non-degradability (Chapman et al. 1998). Sediments tend to act as sinks for heavy metals under accumulating conditions and may subsequently act as sources through releasing metals into water if conditions change (Webster and Ridgway 1994). As an important constituent of aquatic environment, sediments have been the key target in water environmental quality assessment. Hence, sediment assessment should always be used together with water quality assessment to adequately evaluate environment quality of any water body.

Traditionally, sediment contamination was evaluated by comparing the concentrations of each individual compounds with its local geochemical background values (Gambrell et al. 1983; USEPA 2002a). In 1980s, sediment quality criteria (referred to "guidelines", "standards" or "indicators" which did not carry regulatory mandate) were developed for sediment quality assessment to provide reference values (Burton 2002). Some derivation approaches have been trying to incorporate sediment quality criteria (SQC) with biological effects. They have two major categories: an empirical, statistical approach to associate sediment contamination with toxic response (Long and Morgan 1990; Presaud et al. 1993) and a theoretical approach that attempt to account for differences in bioavailability although the equilibrium partitioning approach (Di Toro et al. 1990). Although the traditional sediment contamination assessment approach is still being used nowadays, it provides little insight to the potential risk of adverse biological effects. Empirically based SQCs are derived from field sediment chemistry that pairs with laboratory biological toxic data, but they were based on the total sediment concentrations and do not consider bioavailability of each individual compounds. Theoretically derived SQCs are based primarily on the knowledge of the partitioning of chemicals in the sediment and the toxicity of the dissolved

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fraction of chemicals in the interstitial water. The EqPA surpasses the empirical approaches by resolving two principal technical issues: the varying bioavailability of chemicals in the sediments and the choice of the appropriate biological effect concentration (Di Toro et al. 1991).

In this work, we aimed at using the EqPA to set two types of SQCs in terms of heavy metal concentrations in the sediment, which could be used to establish thresholds in determining the incidence of adverse biological effects on benthic organisms. In addition, a new assessment approach—Sediment Pollution Index, which used the calculated SQCs as reference standards, was established to evaluate the potential risk of biological effects for sediment contamination. The procedures of sediment quality criteria and assessment were applied in the Xiang-jiang River (China) which has suffered serious heavy metal pollution due to industrial effluent and solid waste discharge (Guo 2007; Lei et al. 2010; Mao et al. 2013).

Materials and methods

Study area and sample collection

The Xiang-jiang River derives from the Sea Mountain which is located in the north of Guangxi province, and it is one of the most important tributaries of the Yangtze River in China. The Xiang-jiang River joins the Xiao River in Yongzhou of Hunan province, and then flows eastward through Hengyang, Zhuzhou, Changsha and Yueyang, eventually goes into the Yangtze River after emptying into the Dongting Lake in Xiangyin of Hunan province. The Xiang-jiang River has a length of 856 km with a watershed area of 94,600 km^2. Abundant mineral resources scatter over the sides of the river, including lead (Pb), zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), antimony (Sb), and so on. Lots of mining and smelting activities in this area led to heavy metal pollution in the Xiang-jiang River. The Hengyang section and Zhuzhou section of the River are surrounded by the Shuikoushan industrial park and the Qingshuitang industrial park, respectively. The Yueyang section connects the two rivers (the Xiang-jiang River and the Yangtze River) to the Dongting Lake. Therefore, the study was conducted at Hengyang, Zhuzhou, Yueyang sections of the Xiang-jiang River in April 2010. 37 sample sites were selected, including riverbeds with slow flow, large-scale tributary confluences and drain outlets of pollution sources (Fig. 1).

Analytical methods

Sediment samples were collected from the top 0–5 cm using small size grab mud samplers, and then packed in a polyethylene bag. The samples were transported to our laboratory and stored at 4 °C in the refrigerator for preservation. The samples were freeze dried, homogenized, and crushed to pass through 150-μm nylon sieves (100 meshes), and were used for determination of metal concentration and speciation.

About 0.100 g pretreated sediment was microwave digested using a mixture of acids (3 mL hydrochloric acid + 4.5 mL nitric acid + 1.5 mL hydrofluoric acid). After complete digestion to liquid, the mixture was transferred into a polyfluortetraethylene crucible and added with 1.0 mL perchloric acid. The mixture solution was evaporated to dryness at 250 °C on an electric heating plate. The residue was rinsed with the distilled water, and air died. This procedure was repeated three times. For the third time, 1 mL solution was left and added with 2 mL nitric acid and diluted to 100 mL with distilled water. The concentrations of the metals, including copper, lead, zinc and cadmium in the sediment, were determined using inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500cx).

Interstitial water samples were collected by centrifugation. Fresh sediment samples were centrifuged at 5,000 rpm for 30 min, with 0.45-μm filter membranes. 1 mL interstitial water was added into 2 mL nitric acid and diluted to 100 mL using distilled water. Metals were measured using ICP-MS.

Speciation fraction analyses of copper, lead, zinc and cadmium in the sediment were carried out using the Community Bureau of Reference (BCR) speciation analysis approach (Davidson et al. 1994; Rauret et al. 1999). In recent years, the BCR method has been widely used by many studies for its stability, reproducibility and high accuracy (Quevauviller et al. 1997; Umoren et al. 2007; Jiang et al. 2014). There are four fractions for each metal according to the four-step extraction procedure, which are acetic acid extractable, reducible, oxidizable and residual fraction. Acid volatile sulfide (AVS) in the sediment was analyzed by cold-acid purge-and-trap technique described by Allen et al. (1993), Cornwell and Morse (1987) and Boothman and Helmstetter (1992). The concentrations of simultaneously extracted metals (SEM) in the sediment were determined using ICP-MS. Particle size of sediment was determined using the Mastersizer 2000 laser particle size analyzer. Total organic carbon (TOC) contents in the sediment were analyzed using the method of potassium dichromate described by the Chinese National Environment Protect Government (State Environmental Protection 2002).

A procedural blank was run in parallel with each batch of samples for characteristic and speciation analyses. The relative standard deviation (RSD) of total metal concentration was less than 5 %, and the RSD of metal speciation

Fig. 1 Sampling sites in the Xiang-jiang River, a typical heavy metal polluted zone in Hunan Province

analysis was less than 8 %. The standard reference materials for extractable trace elements (GBW07436) from the National Research Center for Geological Experiment and National Institute of Metrology People's Republic of China were also used, and the recoveries for different forms of metals were controlled between 80 and 120 %.

Results

Sediment quality criteria derived using EqPA

EqPA was based on three empirical hypotheses (USEPA 1989; NOAA 1995), including:

1. Pollutant exchanges quickly and reversibly between sediment phase and interstitial water phase, and the exchange process reaches an equilibrium state eventually.
2. The critical factor controlling sediment toxicity is the concentration of pollutant in the interstitial water.
3. Benthic organisms have similar sensitivity for pollutants to aquatic organisms.

Therefore, the sediment criterion was taken as the concentration of pollutant in the sediment, which was in equilibrium with the concentration in the interstitial water. In addition, the concentration in the interstitial water did not give rise to a concentration in the water that would breach the water quality criterion (WQC) for that pollutant (USEPA 2000; Meng et al. 2006). A partition coefficient (K_p) expressed the relationship between concentration in the sediment (ρ_s) and that in the interstitial water (ρ_{iw}).

$$K_p = \rho_s / \rho_{iw} \tag{1}$$

The equation was modified by setting ρ_{iw} equal to the WQC value for the given pollutant. The corresponding sediment "safe" level, sediment quality criterion (SQC), could be calculated using the following equation.

$$\rho_s = K_p \times \mathrm{WQC} = \mathrm{SQC} \tag{2}$$

In the case of sediment with heavy metal pollution, four metals speciation fractions were divided into acetic acid extractable, reducible, oxidizable and residual fraction by the BCR speciation analysis method. The first three metal fractions in the sediment would possibly take part in the partitioning procedure with interstitial water, so the sum content of the three fractions were the quality concentration of the metal with direct or potential bioavailability in sediment (ρ_s). Residual metal fractions ($[M]_R$) associated with primary minerals did not undergo partitioning with interstitial water (Burton Burton 1993; Chapman et al. 1993), and parts of metals in the acid volatile sulfide ($[M]_{AVS}$) did not undergo equilibrium procedure either, since bivalent metal (Me^{2+}) and bivalent sulfide (S^{2-}) could combine to form sulfide precipitates. Thus, the SQC calculation formula was revised as the following equation:

$$\mathrm{SQC} = K_p \times \mathrm{WQC} + [M]_R + [M]_{AVS} \tag{3}$$

Partition coefficient (K_p)

The concentrations of heavy metals in the sediment and in the interstitial water were significantly correlated with grain size distribution and organic carbon contents in the sediment (Zonta et al. 1994; Marchand et al. 2011). The metal data at sites in the Xiang-jiang River with well-focused fine particle material (<63 μm, including clay and silt) and TOC in the sediment which ranged in 45–75 % and 1.5–3.5 %, respectively, were chosen to calculate K_p values and SQC values in this work. Because they could avoid considering variations of K_p values of metals in the sediment caused by large variations of sediment particles and organic material characteristics. The ρ_s concentrations, ρ_{iw} concentrations $[M]_R$ concentrations and K_p values of copper, lead, zinc and cadmium at sites in the Xiang-jiang River were shown in Table 1. Several additional environmental factors (i.e., pH value, total ion concentration etc.) may also cause uncertainties for K_p values (Huo and Chen 1997). To reduce the probability of false negatives (a toxic sample incorrectly classified as non-toxic) and false positives (a non-toxic sample incorrectly classified as toxic) of SQCs, outliers were tested by box plots (SPSS 16.0) and not considered in the average calculations of K_p.

Water quality criteria (WQC)

The availability of water quality criteria for chemicals of interest is obviously a vital part of the process of designing sediment criteria (McCauley et al. 2000). A series of WQCs for protecting aquatic organisms and human health were published by USEPA (1999, 2002b). Among the WQCs, criterion continuous concentration (CCC) refers to the concentration of pollutant in the surface water under which aquatic organism communities could be exposed indefinitely without adverse impacts. Criterion maximum concentration (CMC) represents a concentration of pollutant in surface water exceeding, which produce unacceptable impacts would be produced in a short time on aquatic organism communities. The CCCs and CMCs of copper, lead, zinc and cadmium were considered as WQCs with chronic and acute biological effects, respectively, to calculate SQCs in the Xiang-jiang River. The calculations for CCCs and CMCs of metals involved water hardness (USEPA 2002b; Xia et al. 2004), and the average water hardness in the Xiang-jiang River was 50.99 μg/L. The calculation results were shown in Table 2.

SQCs in terms of biological toxic effect

It is necessary to take into account the influence of acid volatile sulfide (AVS) in reduced sediment (i.e., lake and reservoir) which could contain AVS (Fang and Xu 2007; Sheng et al. 2013). Nevertheless, the AVS contents in the sediment at most sampling sites in the Xiang-jiang River were under detection limits. This may be due to the oxidized sediment condition with the average of dissolved oxygen of the surface water in the Xiang-jiang River of 8.2 mg/L and the pH ranged from 6.8 to 8.47. Thus the AVS content were under detection limits in such high dissolved oxygen content and shallow water depth environment, and they were ignored in the calculation of SQCs

Table 1 Metal concentration and the calculated partition coefficients in the Xiang-jiang River

Sites	Bioavailable concentration of metal (ρ_s) (μg/g)				Residual concentration of metal ($[M]_R$) (μg/g)				Metal concentration in the interstitial water (ρ_{iw}) (μg/L)				The partition coefficients (K_p) (L/g)			
	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd
HY-1	24.17	52.68	117.04	8.10	14.42	14.93	57.58	0.20	3.99	7.59	6.50	0.61	6.06	6.94	17.99	13.25
HY-3	15.67	31.25	103.75	5.14	8.10	9.95	38.48	0.06	1.50	2.63	4.94	0.40	10.46	11.88	20.99	12.95
HY-4	18.05	54.62	95.08	6.87	20.65	16.34	86.69	0.15	0.02	0.23	ND	ND	*1,042.68*	*236.98*		
HY-5	10.91	52.23	91.67	4.69	16.86	14.55	51.29	0.18	72.60	ND	1.82	3.14	0.15		50.48	1.49
HY-6	13.46	48.81	94.75	6.60	15.93	15.99	62.58	0.17	4.19	2.19	13.95	0.45	3.21	22.30	6.79	14.82
HY-7	12.35	34.36	61.09	3.04	15.38	13.86	25.86	0.06	0.09	ND	ND	0.23	*135.62*			13.15
HY-9	37.27	53.54	97.97	4.83	19.77	16.25	57.97	0.24	4.87	0.77	3.95	0.20	7.66	69.33	24.80	24.61
HY-16	58.51	161.99	493.60	37.06	21.75	27.53	96.84	1.02	ND	ND	ND	ND				
HY-22	63.93	302.40	545.69	100.85	25.67	32.56	136.63	1.13	2.22	1.30	16.59	5.72	*28.74*	*233.16*	32.89	17.64
HY-23	64.11	350.51	345.95	19.61	22.34	38.60	113.93	0.85	2.55	9.72	31.74	4.78	25.14	36.06	10.90	4.11
HY-24	65.69	237.71	592.13	70.63	24.59	31.84	144.80	0.87	4.82	5.20	18.57	5.73	13.62	45.70	31.89	12.32
HY-26	51.95	150.48	340.26	32.11	19.56	29.98	128.13	1.03	10.79	12.91	13.91	8.40	4.81	11.66	24.46	3.82
HY-28	32.83	98.26	230.79	29.76	15.25	23.78	89.44	0.45	3.84	3.14	7.39	2.79	8.55	31.30	31.21	10.66
ZZ-2	26.94	78.28	227.07	22.72	15.53	21.21	63.25	0.43	ND	ND	ND	ND				
YY-2	22.82	56.94	144.72	11.25	10.56	19.75	39.98	0.21	4.80	1.48	5.53	1.69	4.75	38.52	26.19	6.67
YY-3	30.47	74.01	174.14	13.58	13.48	19.28	52.76	0.28	2.59	0.56	1.44	1.22	11.75	132.42	*120.60*	11.15
YY-4	36.22	71.00	175.42	17.39	15.44	21.42	103.41	0.47	ND	ND	ND	ND				
YY-5	43.92	96.34	211.21	16.95	17.94	23.80	109.20	0.51	6.09	ND	0.97	1.32	7.22		*216.91*	12.81
YY-6	34.03	73.84	174.31	11.97	16.28	20.02	93.65	0.52	37.62	1.34	374.10	84.43	0.90	55.02	0.47	0.14
YY-7	25.74	85.09	122.89	7.89	16.33	21.90	99.38	0.34	2.08	ND	6.71	4.79	12.38		18.30	1.64
Average					17.29	21.68	82.59	0.46					8.33	41.92	22.87	10.08

ND not detectable

The data drew italics are outliers tested by box plots in the corresponding column and they are not considered in the average calculations of K_p

Table 2 Sediment quality criteria for heavy metals in the Xiang-jiang River

	Cu	Pb	Zn	Cd
K_p (L/g)	8.33	41.92	22.87	10.08
WQC (CCC) (μg/L)[a, b]	5.04	1.20	52.58	0.15
WQC (CMC) (μg/L)[a, b]	7.12	30.80	66.22	1.05
$[M]_R$ (μg/g)	17.29	21.68	82.59	0.46
SQC-low : SQC (I) (μg/g)	59.26	71.99	1,285.30	2.01
SQC-high : SQC (III) (μg/g)	76.66	1,312.78	1,597.36	11.00
[SQC-low + SQC-high] × 50 %: SQC (II) (μg/g)	67.96	692.39	1,441.33	6.50

[a] USEPA (2002b)

[b] Xia et al. (2004)

by the EqPA in this study. The $[M]_R$ concentration in the Xiang-jiang River was shown in Table 2.

Based on the calculated results of K_p values, WQCs and $[M]_R$ concentrations, the SQCs of copper, lead, zinc and cadmium in the Xiang-jiang River were calculated using Eq. (3), and they were shown in Table 2. Specifically, SQC-Low based on WQC (CCC) was considered as the concentration value in the sediment less than which chronic biological effects on benthic organisms would rarely happen, whereas sediment concentration above SQC-High based on WQC (CMC) would be expected to express acute biological effects on benthic organisms frequently.

The SQCs were divided into three grades according to different biological toxic effects (Table 2): SQC-Low and SQC-High were divided as the first and the third level of SQC, respectively [shorted as SQC (I) and SQC (III) hereinafter]. To further refine the grade of biological toxic effect, (SQC-low + SQC-high) × 50 % value was made as the second level of SQC [shorted as SQC (II) hereinafter]. The metal concentration in the sediment exceeding (SQC-low + SQC-high) × 50 % value would give rise to mid-level chronic biological effect, but no acute effect on benthic organisms.

A method of sediment quality assessment

A number of sediment quality assessment methods have been developed and widely applied to various sediments in the world, i.e. Geoaccumulation Index (Muller 1969; Wang et al. 2014), Enrichment Factor (Chen 1987; Tian et al., 2013), Potential Ecological Risk Index (Hakanson 1980; Lin et al. 2013), Ratio of Secondary and Primary Phase (Chen et al. 1987), Secondary Phase Enrichment Index (Huo et al. 1997) etc. Local geochemical background values or clean compared points have been used often as reference standards by these assessment methods. In this study, a new method called "Sediment Pollution Index" was established to evaluate the potential risk of adverse biological effects on benthic organisms that sediment contaminant would pose. The SQC-low and SQC-high derived using EqPA were chosen as reference standards in the Sediment Pollution Index method, and the result was described as score to make the sediment condition understandable easily by the public.

First, the SPI values of evaluated pollutants at a single site were calculated by Eqs. (4) and (5). Then the maximum of SPI values of evaluated pollutants at a single site was made as the final SPI value of the site. Lastly, the sediment quality condition of the site was judged according to the classification table of sediment quality assessment using the Sediment Pollution Index method (Table 3).

$$SPI(i) = \mathrm{SPI}_l(i) + \frac{\mathrm{SPI}_h(i) - \mathrm{SPI}_l(i)}{\rho_h(i) - \rho_l(i)} \times (\rho(i) - \rho_l(i))$$
$$\rho_l(i) < \rho(i) \le \rho_h(i) \tag{4}$$

When sediment concentration of pollutant (i) was less than the SQC (III) value, equation (4) was used to calculate SPI values. $\rho(i)$ was the concentration of pollutant (i) in sediment. $\rho_l(i)$ was the SQC value of pollutant (i) which was one level below the $\rho(i)$ in Table 2. $\rho_h(i)$ was the SQC value of pollutant (i) which was one level above the $\rho(i)$ in Table 2. $\mathrm{SPI}_l(i)$ was the SPI value which $\rho_l(i)$ corresponded in Table 3. $\mathrm{SPI}_h(i)$ was the SPI value which $\rho_h(i)$ corresponded in Table 3. SPI(i) was the SPI value of pollutant (i) at a single site.

$$\mathrm{SPI}(i) = 30 + \frac{\rho(i) - \rho_4(i)}{\rho_4(i)}.10 \quad \rho(i) > \rho_4(i) \tag{5}$$

When sediment concentration of pollutant (i) exceeded SQC (III), Eq. (5) was used to calculate SPI values. $\rho_4(i)$ was the SQC (III) value of pollutant (i) in Table 2.

$$\mathrm{SPI}(i) = \max[\mathrm{SPI}(i)] \quad i = [1, n] \tag{6}$$

In Eq. (6), the maximum SPI value for "n" kinds of pollutants was confirmed as the final SPI value of the sediment contamination at a single site.

In Table 3, sediment quality assessment using the Sediment Pollution Index method indicated the following result: pollutant concentration in sediment rank I sediment had low toxic risk and rarely gave rise to chronic biological effects on the survival of benthic organisms at a long period of time; pollutant concentration in sediment rank II had moderate toxic risk and would pose light chronic biological effects on their survival; pollutant concentration in sediment rank III sediment had considerable toxic risk and would not cause acute, but serious chronic biological effects on benthic organisms; pollutant concentration in sediment rank IV sediment had high potential toxic risk and would impact the health of benthic organisms with

Table 3 Classification of Sediment quality assessment using the Sediment Pollution Index method at a single site

SQC	SQC (I)	SQC (I)–SQC (II)	SQC (II)–SQC (III)	SQC (III)
SPI range	SPI ≤10	10 < SPI ≤ 20	20 < SPI ≤ 30	SPI >30
Sediment rank	I	II	III	IV
Sediment quality condition	Good	Moderate	Bad	Very bad
Sediment risk	Low toxic risk	Moderate toxic risk	Considerable toxic risk	High potential toxic risk

acute biological effects in a short period of time. Different colors will be used to represent the different levels of sediment quality evaluation; that is to say, sediment in good, moderate, bad and very bad condition will be represented by green, yellow, blue and red colors, respectively.

Discussion

Evaluation of SQCs in the Xiang-jiang River

It was of interest to compare SQCs in the Xiang-jiang River derived using EqPA with other freshwater sediment criteria [i.e., threshold effect level (TEL), probable effect level (PEC), threshold effect concentration (TEC) and probable effect concentration (PEC)], which were empirically based on historical sediment and biological effects field databases (Table 4). With the exception of zinc, the SQC-low values of copper, lead and cadmium in the Xiang-jiang River were in the same orders of magnitude with TEL and TEC. Moreover, the SQC-low values of metals in the Xiang-jiang River were also in the same order of magnitude with other freshwater basins' SQCs in China (i.e., the Liao-he River, the Han-jiang River, the Le-anjiang River and the Tai-hu Lake in Table 4), which were calculated in the same way. These comparisons suggested that the EqPA could provide meaningful sediment quality criteria.

In Table 4, the SQC-Low value of zinc in the Xiang-jiang River was in the same order of magnitude with the Le-anjiang River and the Tai-hu Lake, but it was much higher than the levels found in the Liao-he River and the Han-jiang River. This may be caused directly by the equilibrium partitioning coefficient of zinc which varied considerably from the Xiang-jiang River to other river basins. The K_p value of zinc in the Xiang-jiang River was local, and the calculated SQC-low, SQC-high values of zinc in the Xiang-jiang River were credible. For many other factors influencing the K_p values in the sediments, further research should be done to implement the stable K_p values and to make the SQCs more accurate.

As we know, SQC-High represented the threshold which would pose acute biological effects on benthic organisms, whereas PEL and PEC represented the concentrations which may induce possible or moderate adverse effects. Theoretically, SQC-High values should be significant higher than PEL and PEC values for causing serious biological effects in a short period of time. In Table 4, SQC-High values of metals in the Xiang-jiang River were much higher than PEL and PEC values, with exception of copper. The low SQC-High value of copper in the Xiang-jiang River may be caused by the low WQC (CMC) value of copper.

The SQC values derived using EqPA were slightly higher than that by empirical approaches, and they varied tremendously in different river basins. These differences may be attributed to different sediment factors (i.e., sediment pollution degree, sediment geochemical characteristic, sediment pollutant bioavailability and toxicity), calculation methods and the objectives in dealing with contaminated sediments, etc. (Chen et al. 2005). False negatives and false positives may occur easily and regional restrictions may happen too. The SQC values derived using EqPA were best used as references to indicate sediment pollution, rather than restriction criteria during judgment and decision-making processes, because the SQC value of single metal did not consider the interactions among metals for combined contamination effects (Jiang et al. 2013). The EqPA-based SQCs could be linked to a large water quality database and provide chances to judge whether sediment pollutant level led to adverse effects on the benthic organisms.

Sediment quality assessment for the Xiang-jiang River by Sediment Pollution Index

By definition, the SPI values for copper, lead, zinc and cadmium at sites of the Xiang-jiang River were calculated and shown in Fig. 2.

Copper: SPI values of copper in the Zhu-zhou, Yue-yang sections were lower than 10, but that in the middle reach of Heng-yang section (HY-11, HY-15-HY-18 sites) and in the downstream of Heng-yang section (HY-22-HY-25 sites) were higher than 30. These suggested that copper accumulation in the sediment in the middle and downstream reaches of Heng-yang section should be recognized, especially due to their high risk of biological effects on benthic organisms.

Table 4 Comparison of SQCs in the Xiang-jiang River by other freshwater sediment quality criteria (μg/g)

	Cu	Pb	Zn	Cd
SQC-Low in the Xiang-jiang River, China	59.26	71.99	1,285.30	2.01
TEL, Canadian Freshwater Sediment Guidelines[a]	35.7	35	123	0.6
TEC, Consensus-based Sediment Guidelines for Freshwater[b]	31.6	35.8	121	0.99
SQCs in the Liao-he River, China[c]	52.8	18.9	177.7	5.42
SQCs in the Han-jiang River, China[d]	62	112	640	55
SQCs in the Le-anjiang River, China[e]	192–983	45–282	251–3,222	2–40
SQCs in the Tai-hu Lake, China[f]	52.3–281.0	21.2–307.4	399.7–1,659.0	\
SQC-High in the Xiang-jiang River, China	76.66	1,312.78	1,597.36	11.00
PEL, Canadian Freshwater Sediment Guidelines[a]	197	91.3	315	3.53
PEC, Consensus-based Sediment Guidelines for Freshwater[b]	149	128	459	4.98

[a] Smith (1996)

[b] MacDonald et al. (2000)

[c] Deng et al. (2011)

[d] Huo et al. (1997)

[e] Liu and Tang (1998)

[f] Hou et al. (2012)

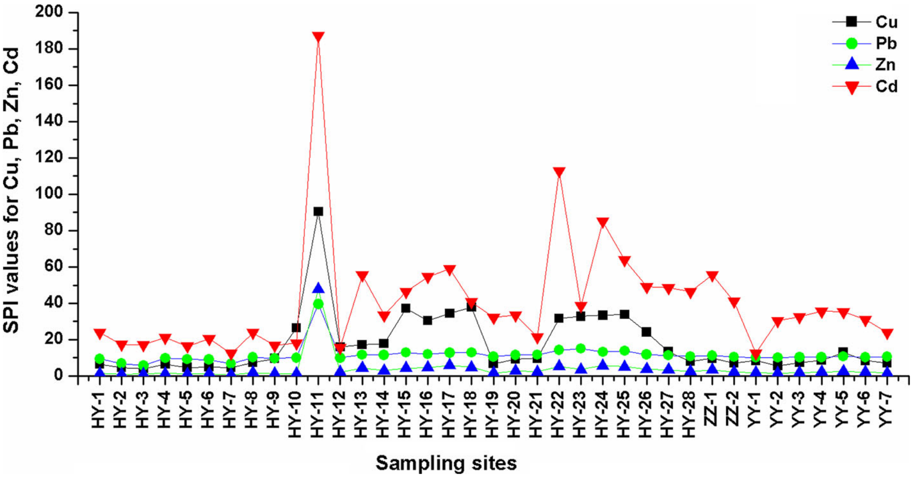

Fig. 2 The SPI values for Cu, Pb, Zn and Cd at sites of the Xiang-jiang River

Lead: Except for HY-1-HY-7, HY-9 and HY-11 site which was located in the Heng-yang section, SPI values of lead at other sites of Heng-yang, Zhu-zhou, Yue-yang sections in the Xiang-jiang River were ranged from 10 to 20. This meant that lead contamination in the sediment of the Xiang-jiang River had middle toxic risk and would cause moderate biological effects on benthic organisms at a long period of time.

Zinc: Except for HY-11 site which was located in the Heng-yang section, SPI values of zinc at other sites of Heng-yang, Zhu-zhou, Yue-yang sections in the Xiang-jiang River were less than 10. This meant that zinc contamination in the sediment of the Xiang-jiang River had low toxic risk and would not cause chronic biological effects on benthic organisms at a long period of time.

Cadmium: With exception of sites in the upstream of Heng-yang section (HY-1-HY-10 sites), SPI values of cadmium in the middle and downstream reaches of the Xiang-jiang River were mostly higher than 30. This indicated that acute and unacceptable biological effects on benthic organisms caused by cadmium contamination in the sediment may occur frequently.

When comparing with copper, lead and zinc, SPI values of cadmium in the Xiang-jiang River were the highest. Therefore, the final SPI value for a single site was mainly contributed by the SPI value of cadmium (Fig. 4). The final SPI values in the middle and downstream reaches of Heng-yang section and Zhu-zhou, Yue-yang sections in the Xiang-jiang River were generally in sediment rank IV. This suggested that sediment

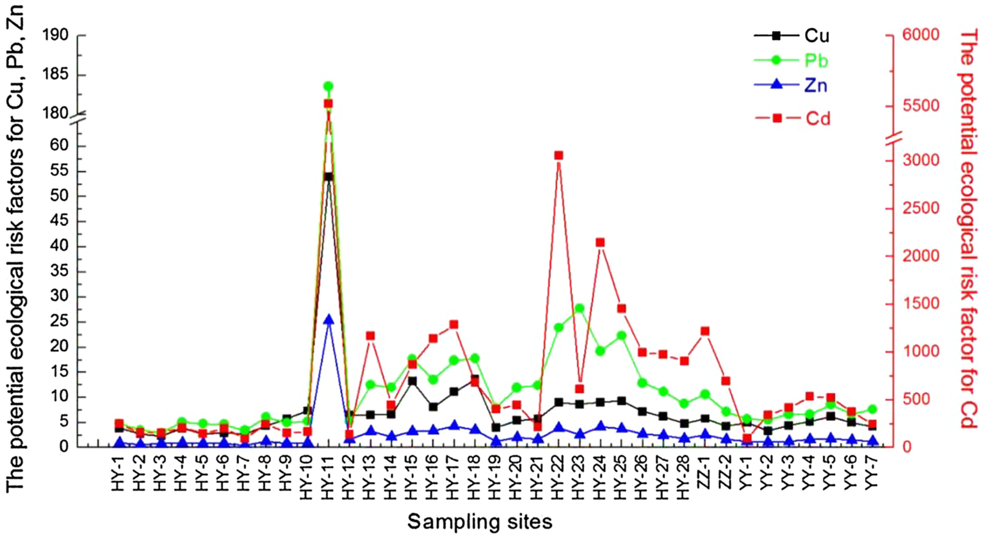

Fig. 3 The potential ecological risk indices (PI) for Cu, Pb, Zn and Cd at sites of the Xiang-jiang River Note: PI < 40 represents low potential ecological risk caused by single contaminant (Cu, Pb, Zn and Cd), 40 < PI < 80 moderate potential ecological risk, 80 < PI < 160 considerable potential ecological risk, 160 < PI < 320 highly potential ecological risk, PI > 320 very high ecological risk at hand for the substance in question

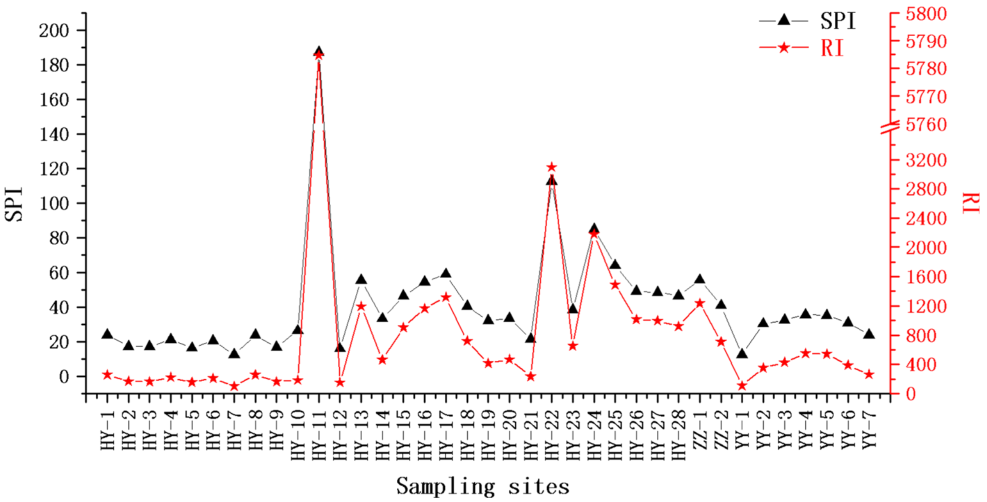

Fig. 4 The final SPI values and the comprehensive potential ecological risk indices (RI) at sites of the Xiang-jiang River. The final SPI value at a single site is the maximum of SPI values for Cu, Pb, Zn and Cd. The RI at a single site is the sum of the potential ecological risk factors for Cu, Pb, Zn and Cd. RI < 150 represents low toxic risk caused by sediment contamination, 150 < RI < 300 moderate ecological risk, 300 < RI < 600 considerable ecological risk, RI > 600 very high ecological risk

contamination in these areas had high risk of biological effects on benthic organisms.

It can be seen from Fig. 4 that SPI values of copper, lead, zinc and cadmium at site HY-11 were the highest of all sites with values higher than 30. HY-11 site is about 4 km from Shui-koushan industrial park in Heng-yang section, and close to the confluence of a southern tributary, Chong-ling River. The Shui-koushan industrial park is located in the center of the Shui-koushan mining area which contains abundant lead, zinc, cooper resources, etc. Heavy metals discharged from industrial sources were mainly adsorbed onto suspended solids (SS), and then SSs associated heavy metals were settled at the bottom of the river. The amounts of SSs which adsorbed heavy metals decreased gradually along with the stream due to settling into sediments; therefore, the sediments at sites closer to pollution sources had higher contents of heavy metals. And there was a gradual decrease in contents of heavy metals in the sediment at the downstream sites. HY-22 site was located 1.5 km away from an industrial company that mainly produced lithopone. Thus SPI values of metals at the HY-22 site were higher than those of other sites nearing it. This suggested that sediment contamination of metals in the Shui-koushan industrial park were expected to pose serious adverse biological effects on benthic organisms frequently and effective remedial actions should be implemented as soon as possible.

Sediment quality assessment for the Xiang-jiang River by Potential Ecological Risk Index

To confirm the results evaluated by the Sediment Pollution Index method, the Potential Ecological Risk Index method was also used in this work to evaluate sediment quality of the Xiang-jiang River. The metal concentrations in the sediment of rivers and lakes in Europe and America before the industrial age (copper, lead, zinc, cadmium respectively were 50, 70, 175 and 1 μg/g) were used as background values, and the toxicity response parameters of copper, lead, zinc, cadmium were 5, 5, 1 and 30, respectively (Hakanson 1980). The assessment results of the Xiang-jiang River by the Potential Ecological Risk Index method were shown in Fig. 3. Notably, the potential ecological risk indices (PI) of cadmium at sites of the Xiang-jiang River were considerably higher than copper, lead and zinc. These were consistent with the assessment results by the Sediment Pollution Index method. Enrichment and high ecological risk of cadmium in the sediments were also found in the Liaodong Bay (Zhao et al. 2014), the Hunhe River (Guo and He 2013) and the Port Klang coastal area (Sany et al. 2013), etc.

The Xiang-jiang River basin has abundant mines and developed industries of mining, smelting, pigment, plating, etc. Industrial effluent is the most important role of metals pollution in the Xiang-jiang River. Even though the concentration of cadmium in the industrial effluent was not higher than those of other metals, the SPI value and PI value of cadmium at sites of the Xiang-jiang River were higher than other metals. This could be attributed to that cadmium had active metal property (Li et al. 2013), strong toxicity, and much lower water/sediment background value, water/sediment quality criteria or standard than other metals.

The comprehensive potential ecological risk indices (RI) in the Xiang-jiang River were shown in Fig. 4. The two methods had similar assessment results. The Potential Ecological Risk Index method can evaluate the potential ecological risk posed by sediment contamination, while the Sediment Pollution Index method can make further evaluation than the Potential Ecological Risk Index method in subdividing biological effects on benthic organisms into acute toxic and chronic toxic.

Conclusion

USEPAs fresh water quality criteria [criterion continuous concentration (CCC), criterion maximum concentration (CMC)] were referenced to derive sediment quality criteria (SQC-low and SQC-high) of the Xiang-jiang River. If metal concentrations in the sediments were less than SQC-low values, chronic biological effects on benthic organisms would rarely happen. Acute biological effects would be detected frequently as metal concentrations in the sediments above SQC-high values. And furthermore, the SQC-low and SQC-high values derived by EqPA could provide related references for setting sediment quality standards. The SQC-low values of copper, lead, zinc, cadmium in the Xiang-jiang River were 59.26, 71.99, 1,285.30 and 2.01 μg/g, respectively, and the SQC-High values were 76.66, 1,312.78, 1,597.36 and 11.00 μg/g, respectively. When comparing the SQCs in the Xiang-jiang River with other studies' criteria, a consensus in the orders of magnitude was reached.

Using the calculated SQC values as reference standards, Sediment Pollution Index method was established and applied to evaluate the risk of adverse biological effect on benthic organisms caused by sediment contamination in the Xiang-jiang River. The assessment results of Sediment Pollution Index method showed good agreement with that using the Potential Ecological Risk Index method. It was revealed that cadmium contaminant caused higher risk of acute biological effects on benthic organisms than copper, lead and zinc in the sediment of the Xiang-jiang River, especially in the middle and downstream reaches of Heng-yang section and Zhu-zhou, Yue-yang sections.

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