

# Assessment of metal toxicity and development of sediment quality guidelines using the equilibrium partitioning model for the Three Gorges Reservoir, China

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**Abstract** The impoundment of the Three Gorges Reservoir (TGR) in China influences the quality of the water supply. Surface sediment samples from the TGR mainstream and three tributaries were collected. Acid volatile sulfide (AVS), simultaneously extractable metals (SEMs), and the fraction of organic carbon ( $f_{oc}$ ) were used to assess the toxicity of heavy metals. Sediment quality guidelines (SQGs) were established using the equilibrium partitioning approach. The results showed that the surface sediments were found to be oxic or suboxic. AVS concentrations in sediments were relatively low, below SEM concentrations. The  $[SEM] - [AVS]$  model indicated that all sediments possibly have adverse effects on aquatic life. However,  $([SEM] - [AVS])/f_{oc}$  predicted no adverse biological effects in some areas of the Meixi and Caotang Rivers, while adverse effects to aquatic life were uncertain for the other sediments. The partitioning coefficients, water quality criteria, and residual metals in the sediments were the main factors influencing the SQGs for the TGR, while the metals bound to AVS had a negligible effect.

The normalized TGR SQGs were all much higher than the existing standards except for cadmium and copper. The differences might be attributed to the approaches used for derivation of SQGs and the physical and chemical characteristics of the sediments.

**Keywords** Heavy metal · Sediment · Acid volatile sulfide · Simultaneously extractable metals · Equilibrium partitioning · Sediment quality guideline · Three Gorges Reservoir

## Introduction

Heavy metals are an ecological concern in aquatic ecosystems because of their non-degradable, persistent nature, which causes them to accumulate in sediments (Gao et al. 2013; Fu et al. 2014). Hence, sediments have become the main reservoir for metal contaminants (Louriño-Cabana et al. 2011). However, when the aquatic environment changes (pH, Eh, etc.), sediments may become a source of heavy metals, impacting water quality and posing risks to aquatic organisms (Morgan et al. 2012; Zhuang and Gao 2013).

Several approaches have been developed to assess the impacts of heavy metals in sediments to the environment over the past 30 years (Wenning 2005). Traditionally, total concentrations of metals have been compared to numeric sediment quality guidelines (SQGs). However, studies have increasingly shown that the total heavy metal concentration alone may not accurately reflect ecological effects on aquatic organisms (Campana et al. 2013; Vink 2002). The chemical form of heavy metals in sediments determines their solubility and bioavailability in the aquatic environment (Yu et al. 2001).

As a major chemical component of sediments, acid volatile sulfide (AVS) plays a significant role in controlling the activity and bioavailability of metals in interstitial water (Gao et al.

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2013; Prica et al. 2008). Several divalent transition metal cations (Cd, Cu, Ni, Pb, and Zn) react with sulfide to form highly insoluble metal sulfides that have minimal biological availability (Ankley et al. 1996; Di Toro et al. 1990; USEPA 2004). AVS is operationally defined as the amount of sulfide that can be extracted with cold hydrochloric acid (6 M HCl). Metals in the sediments extracted during this process are called simultaneously extractable metals (SEMs), including mainly Cd, Cu, Ni, Pb, and Zn (Di Toro et al. 1990). Comparison of the molar concentration of AVS ([AVS],  $\mu\text{mol/g}$ ) to the sum of SEM molar concentrations ([SEM],  $\mu\text{mol/g}$ ) has been used to evaluate the potential effects of metals on benthic species in anaerobic sediments. When  $[\text{SEM}]/[\text{AVS}] > 1$  or  $[\text{SEM}] - [\text{AVS}] > 0$ , heavy metals may be toxic, whereas acute toxicity is less likely when  $[\text{SEM}]/[\text{AVS}] < 1$  or  $[\text{SEM}] - [\text{AVS}] < 0$  (Ankley et al. 1996; Di Toro et al. 1990, 2005). However, this approach has limitations. When  $[\text{SEM}]/[\text{AVS}] > 1$  or  $[\text{SEM}] - [\text{AVS}] > 0$ , heavy metal toxicity can be overestimated. Other constituents of the sediments such as organic matter can also combine with free metal ions, thereby reducing their bioavailability and toxicity (Burton et al. 2005). Experimental results have shown that the fraction of organic carbon ( $f_{\text{oc}}$ ) in sediments can be used to normalize the difference between SEM and AVS, i.e.,  $([\text{SEM}] - [\text{AVS}])/f_{\text{oc}}$  (Di Toro et al. 2005; Burton et al. 2005; Nguyen et al. 2011; Costello et al. 2012; USEPA 2005).

SQGs are a fundamental component of all sediment quality assessment frameworks (Simpson et al. 2011). A number of SQGs have been developed using various methods to predict toxicity in the aquatic environment under regulatory programs (USEPA 2004). These SQGs can be categorized into empirical and mechanistic groups (Zhong et al. 2013). Empirical SQGs have been derived from existing datasets of sediment chemistry and corresponding adverse biological effects (Chapman et al. 1999; Li et al. 2014b, c). Among the empirical SQGs, the threshold/probable effect levels (TELS/PELs) and the effects range low/median (ERLs/ERMs) are the most commonly used worldwide to assess sediment toxicity (Li et al. 2014b, c). China also established marine SQGs in 2002. Other SQGs have been developed using a mechanistic approach; the US Environmental Protection Agency (USEPA) equilibrium partitioning (EqP) approach is representative of these methods for selected metals (Ankley et al. 1994). The EqP model is based on the assumption that the toxicity of metals is associated with their interstitial water concentrations taking into account the influence of sulfides and organic carbon in sediments (Burton et al. 2005). Water quality criteria (WQC) can be applied to interstitial water contaminants, and SQGs can be calculated based on the concentration of contaminants in the sediments that is in equilibrium with the WQC concentration in the interstitial water (Chen et al. 2007). The ratio of the contaminant concentration in the sediment solid phase ( $C_s$ ) to that in interstitial water ( $C_{\text{iw}}$ ) is defined as the partitioning

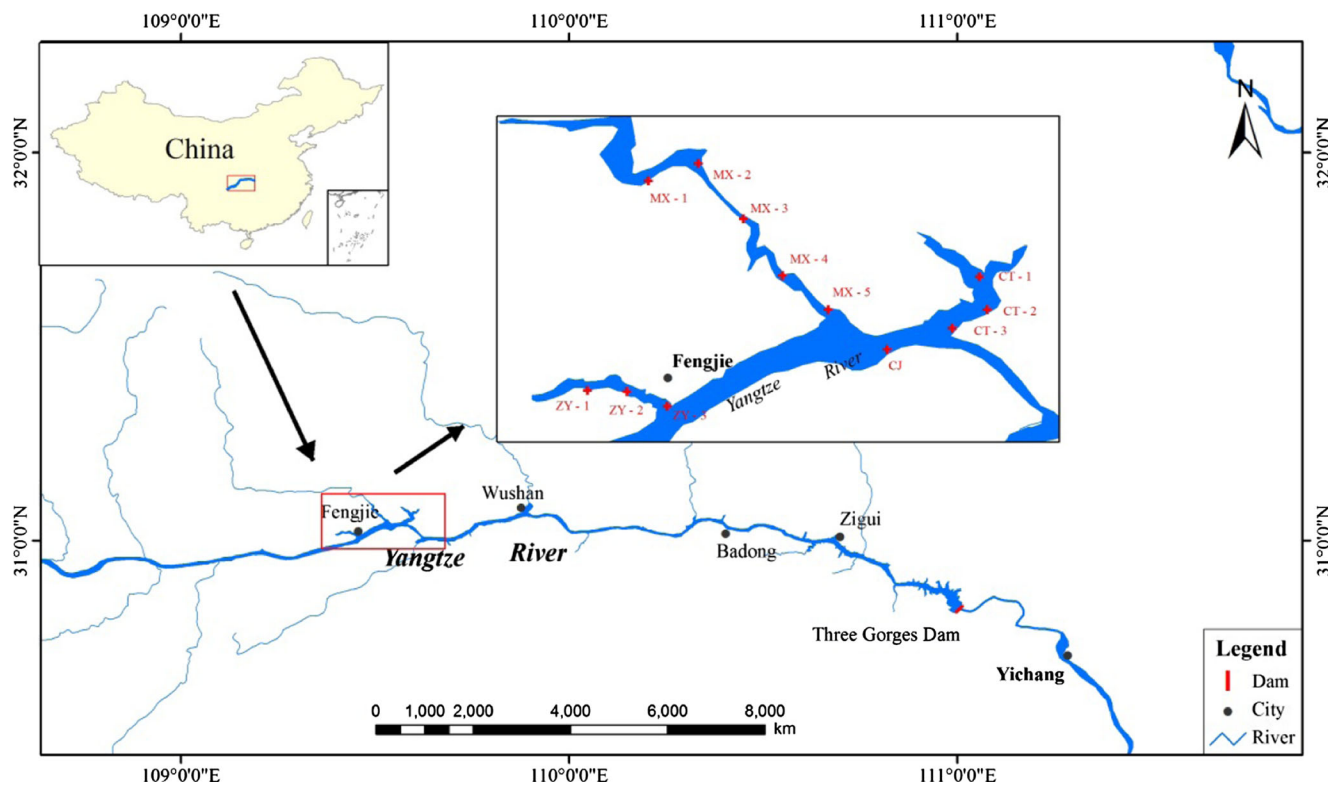
coefficient ( $K_p$ ). However, this method is less developed and few EqP-based SQGs for metals are currently available. SQGs derived using the EqP model depend on the  $K_p$  and AVS, SEM, total organic carbon (TOC), and other binding factors (Chen et al. 2007).

The Yangtze River in China is the longest river in Asia and the third longest in the world (Yang et al. 2009). The Three Gorges Reservoir (TGR) is located at the outlet of the upper Yangtze River, with a surface area of 1080 km<sup>2</sup>, a drainage area greater than  $1.0 \times 10^6$  km<sup>2</sup> (Huang et al. 2006; Ye et al. 2011), and a storage capacity of 39.3 billion m<sup>3</sup> in 2009 (Tang et al. 2014). The TGR is one of the largest man-made reservoirs in the world. As the most important freshwater resource in China, the TGR greatly affects the ecological environment of the Yangtze River system and the quality of the water supply. However, the aquatic environment downstream of the Yangtze River and its tributaries and heavy metal biological toxicity links to the highly dynamic hydrologic regime after impoundment are not well understood (Feng et al. 2013). In recent years, heavy metals in the TGR have caused widely public concern; traditional total heavy metal concentrations, the geoaccumulation index, and potential ecological risk index demonstrated the existence of potential risks to local residents (Tang et al. 2014; Wang et al. 2012). These studies have inadequate scientific evidence to evaluate toxicity and bioavailability. In this study, we collected surface sediment samples from the TGR and determined the heavy metal concentrations (Cu, Cd, Pb, Zn, and Ni) and the concentrations of AVS, SEM, and TOC. The objectives of this study were to (1) assess the toxicity of the heavy metals in sediments (Cu, Cd, Pb, Zn, and Ni) using AVS, SEM, and TOC and (2) develop SQGs using the USEPA EqP model.

## Materials and methods

### Sample collection

Sediments were collected from the Yangtze River mainstream and three tributaries (Zhuyi River (ZY), Meixi River (MX), and Caotang River (CT)) to the TGR in July 2014 (Fig. 1). At each sampling site, samples were taken using a core sampler (K-B type, Wildco, USA) near the middle of the stream. Surface sediment was collected into clean polyethylene bags and treated immediately on returning to the laboratory. The sediment samples were wet-sieved through an acid-cleaned 63- $\mu\text{m}$  mesh nylon sieve to obtain the chemically active material, dried at 40 °C to a constant weight, and ground in an agate mortar to ensure homogeneity.



**Fig. 1** Sampling sites for the Three Gorges Reservoir

**Acid volatile sulfide and simultaneously extracted metals analysis**

AVS and SEM were analyzed within 2 weeks of sample collection by optimizing the methods described by Allen et al. (1993) and Brouwer and Murphy (1994). Briefly, sediments were homogenized gently in a N<sub>2</sub>-filled glove bag. The experimental setup involved a 250-mL round-bottom reaction flask sequentially connected to a scrubbing bottle containing 30 mL of 0.5 M NaOH solution to trap the evolved gases. The experimental apparatus was purified for 20 min with high-purity N<sub>2</sub> at a flow rate of 60 mL/min to remove internal oxygen. About 5 g of the wet sediment sample was added to the reaction flask and sparged for another 10 min with N<sub>2</sub> at a flow rate of 60 mL/min. Next, 20 mL of HCl (1+1) solution was quickly injected into the round-bottom reaction flask to release H<sub>2</sub>S. The sediment suspension was stirred for 50 min under continuous N<sub>2</sub> at a flow rate of 40–60 mL/min. The H<sub>2</sub>S was subsequently collected in NaOH solution. The dissolved sulfide concentration in the NaOH solution was determined using the methylene blue colorimetric method at 665 nm (Cline 1969). The acidic extracts remaining in the flask after extraction were filtered through a 0.45-µm membrane for SEM analysis. SEM analyses for Cd, Cu, Ni, Pb, and Zn were carried out using inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan DRC-e). [SEM] was calculated as the sum of the concentrations of all simultaneously extracted

metals, using the equation [SEM] = [SEM<sub>Cu</sub>] + [SEM<sub>Cd</sub>] + [SEM<sub>Pb</sub>] + [SEM<sub>Ni</sub>] + [SEM<sub>Zn</sub>] (Di Toro et al. 2005). Quality control of AVS extraction was assured by adding known amounts of sulfide to wet sediments. The mean recovery of AVS was 90 %.

**Metal and conventional analysis**

The water content of the sediments was determined gravimetrically. About 5–10 g of wet sediment was dried at 105 °C to a constant weight. The granularity of each sample was analyzed using a particle size analyzer (Mastersizer 2000; Malvern, UK) with the ability to analyze a particle size range of 0.02–2000 µm. The particle size ranges used were <4 µm (clay), 4–63 µm (silt), and >63 µm (sand) (Gao and Chen 2012). TOC in decarbonated sediments was analyzed using an Elementar Vario MACRO Cube CHNS analyzer.

A modified European Community Bureau of Reference (BCR) sequential extraction method was used to characterize four metal fractions in sediments. Briefly, about 0.8 g of dried sediment was weighed into a set of centrifuge tubes and subjected to a series of extractions. The four fractions were acid-exchangeable (F1), reducible (F2), oxidizable (F3), and residual (F4) metals. The total metal concentration in the sediment was measured using acid digestion. Heavy metal concentrations in interstitial water were measured after centrifugation. Sediment samples were placed in centrifuge tubes, centrifuged

at 4000 rpm for 20 min, and filtered through a 0.45- $\mu\text{m}$  membrane. ICP-MS was used to determine the heavy metal concentrations, including Cu, Zn, Cd, Pb, and Ni in the digest, BCR extract, and interstitial water.

All results are expressed on a dry weight basis. All reagents were of analytical or guaranteed grade and all materials (bottles, tubes, etc.) were soaked in 20 %  $\text{HNO}_3$  (v/v) and cleaned with de-ionized water before use.

### Water quality criteria

In accordance with the USEPA approach, the freshwater criteria for heavy metals were calculated as a function of hardness in the water column (USEPA 2009). There are two levels of criteria: the criterion maximum concentration (CMC) and the criterion continuous concentration (CCC). The CMC is the highest concentration of a substance that can be present in surface water for a short time without unacceptable adverse effects to the aquatic community. The CCC is the highest concentration of a substance that can be present in surface water over a long-term exposure without unacceptable adverse effects to aquatic organisms. The CCC is protective of most aquatic communities, so we selected the CCC as the WQC for derivation of SQGs. National quality standards (Grade I and II in GB3838-2002) for freshwater recommended by the State Environmental Protection Administration of China (SEPAC) (2002) were also adopted as protective levels for benthic organisms. The WQC formulas and related parameters are shown in Supplementary Table S1.

### Sediment quality guideline calculation methods

Consistent with the EqP model, SQGs were calculated as follows (USEPA 1995):

$$SQG = K_p \times WQC \quad (1)$$

$$K_p = \frac{C_s}{C_{iw}} \quad (2)$$

$$C_s = C_T \times (1-A\%) \quad (3)$$

where  $WQC$  is the selected water quality criterion (mg/L),  $K_p$  is the partitioning coefficient,  $C_s$  is the concentration of the metal in the sediment solid phase (mg/kg),  $C_{iw}$  is the concentration of the metal in the interstitial water ( $\mu\text{g/L}$ ),  $C_T$  is the total concentration of the metal in the sediment (mg/kg), and  $A$  is the percentage of residual heavy metals in the sample (%).

Heavy metals in the residual state have very low bioavailability. According to Di Toro et al. (1992), AVS can bind several divalent metals and forms insoluble sulfide complexes with minimal biological availability. Therefore, the

normalized SQGs for these metals can be calculated as follows:

$$SQG = K_p \times WQC + M_{Ri} + M_{AVSi} \quad (4)$$

$$M_{AVSi} = AVS \times M_i \frac{C_{Ti}}{\sum_{i=1}^{n=5} C_{Ti}} \quad (5)$$

where  $M_{Ri}$  is the residual concentration of the metal in the sample (mg/kg),  $M_{AVSi}$  is the concentration of the metal bound to AVS (mg/kg),  $[AVS]$  is the concentration of AVS ( $\mu\text{mol/g}$ ), and  $M_i$  is the atomic weight of the metal (Cu, Cd, Pb, Zn, or Ni).

## Results and discussion

### Acid volatile sulfide and simultaneously extractable metal concentrations

Concentrations of AVS, SEM, and acid-extractable metals in surface sediments are presented in Table 1. Generally, AVS concentrations at the river mouth were higher than upstream and concentrations in the mainstream were higher than in the tributaries. Relatively low AVS concentrations were found in the study area, within the range of 0.0034–0.0572  $\mu\text{mol/g}$ , indicating oxic or suboxic environments in the surface sediments. Li et al. (2014b) and Ji et al. (2011) measured AVS in coastal sediments and found that large areas of sediments were oxic or suboxic, similar to our results. All of the surface sediments had relatively low AVS concentrations, suggesting  $[SEM] > [AVS]$ .

Zn and Cu were highest among the acid-extractable metals in the samples (Table 1), contributing approximately 78.41–84.5 % to the total SEM. In contrast, the much more toxic element Cd accounted for <0.5 % of the SEM. Concentrations of acid-extractable trace metals fell in the following order:  $[SEM_{Cd}] < [SEM_{Pb}] \approx [SEM_{Ni}] < [SEM_{Cu}] < [SEM_{Zn}]$ . These results were consistent with study of Bohai and the Yellow Sea (Gao et al. 2013).

### Assessment of sediment heavy metal toxicity using equilibrium partitioning method

SEM can react with AVS to form insoluble metal sulfides that are not bioavailable to benthic organisms. According to the USEPA, the difference between the sum of the SEM concentrations of five heavy metals (Cu, Cd, Pb, Zn, and Ni) and the AVS concentration is one method for evaluating metal toxicity in sediments (USEPA 2004). Samples are classified into the following three tiers: Tier 1,  $[SEM] - [AVS] > 5$ , adverse effects on aquatic life are probable; Tier 2,  $0 < [SEM] - [AVS] < 5$ , adverse effects on aquatic life are

**Table 1** Concentrations of AVS (μmol/g dw), SEM (μmol/g dw), and acid-extractable metals in surface sediments

Sampling site	[AVS]	[SEM <sub>Cu</sub> ]	[SEM <sub>Cd</sub> ]	[SEM <sub>Pb</sub> ]	[SEM <sub>Zn</sub> ]	[SEM <sub>Ni</sub> ]	[SEM]	[SEM]–[AVS]	([SEM]–[AVS])/f <sub>oc</sub>
ZY-1	0.0369	0.3593	0.0056	0.0998	0.8875	0.1706	1.5228	1.4859	241.28
ZY-2	0.0324	0.3687	0.0069	0.1114	0.8168	0.1512	1.4550	1.4226	177.56
ZY-3	0.0414	0.3623	0.0070	0.1690	1.0054	0.1441	1.6878	1.6464	137.34
MX-1	0.0280	0.1476	0.0025	0.0616	0.4523	0.1011	0.7650	0.7370	48.53
MX-2	0.0384	0.2431	0.0038	0.0732	0.6067	0.1140	1.0409	1.0025	75.25
MX-3	0.0194	0.1744	0.0027	0.0685	0.5065	0.0822	0.8344	0.8151	42.60
MX-4	0.0218	0.5212	0.0042	0.1536	0.7500	0.1285	1.5574	1.5356	134.56
MX-5	0.0559	0.4057	0.0069	0.1651	1.2239	0.1458	1.9473	1.8915	83.70
CT-1	0.0034	0.3430	0.0050	0.1055	0.6763	0.1530	1.2828	1.2794	85.22
CT-2	0.0198	0.3843	0.0077	0.1349	0.9160	0.1469	1.5898	1.5700	143.46
CT-3	0.0338	0.4159	0.0084	0.2040	1.4613	0.1455	2.2351	2.2014	182.88
Yangtze	0.0572	2.2133	0.0094	0.4475	2.1184	0.3376	5.1263	5.0691	626.14

$$[SEM] = [SEM_{Cu}] + [SEM_{Cd}] + [SEM_{Pb}] + [SEM_{Zn}] + [SEM_{Ni}]$$

possible; and Tier 3, [SEM]–[AVS]<0, no adverse effects are observed (USEPA 2004). All of the samples in this study were classified into Tier 2, except the Yangtze site, which was Tier 1 at 5.0691. Thus, heavy metals in surface sediments in all of the samples possibly have adverse effects on aquatic life.

However, considering that there are many heavy metal binding phases in sediments, not all sediments with [SEM]–[AVS]>0 exhibit adverse effects to aquatic life (Burton et al. 2005; Brix et al. 2010; De Jonge et al. 2012). Therefore, USEPA has developed a complementary method for evaluating metal toxicity more accurately. This approach incorporates TOC content in the sediments using the formula ([SEM]–[AVS])/f<sub>oc</sub> (μmol/g OC). The results are also classified into three tiers: Tier 1, adverse biological effects may occur when ([SEM]–[AVS])/f<sub>oc</sub>>3000; Tier 2, adverse effects are uncertain when ([SEM]–[AVS])/f<sub>oc</sub>=130–3000; and Tier 3, adverse effects are unlikely when ([SEM]–[AVS])/f<sub>oc</sub><130 (USEPA 2005). According to this approach, the surface sediments at sites Meixi 1, 2, 3, and 5 and Caotang 1 fell into Tier 3 indicating no adverse biological effects, whereas the [SEM]–[AVS] criterion predicted possible adverse effects on aquatic life. Adverse effects to aquatic life were uncertain (Tier 2) for all of the other sites.

**Analysis of variables used to derive sediment quality guidelines**

Using the EqP method, the SQGs are affected by the K<sub>p</sub>, WQC, M<sub>AVS</sub>, and M<sub>R</sub>; of these, the K<sub>p</sub> is one of the most important (Chen et al. 2007). There are two methods for determining the K<sub>p</sub>. The K<sub>p</sub> can be calculated using a surface complexation model (Wang et al. 1997) or by directly measuring metal concentrations in interstitial water and the

sediment solid phase. We selected the latter method because it minimizes potential errors by reflecting the actual physical and chemical conditions in the sediments (Huo and Chen 1997). C<sub>s</sub> and C<sub>iw</sub> are listed in Supplementary Table S2. Metal concentrations in interstitial water were low compared with sediment concentrations. The higher metal concentrations in the solid phase and lower concentrations in the interstitial water resulted in high K<sub>p</sub> values (Table 2). K<sub>p</sub> values for Pb and Zn were particularly high, 1–2 orders of magnitude larger than in previous studies (Chen et al. 2007; Deng et al. 2011). This higher K<sub>p</sub> can be explained by the distribution of particle sizes (Chen et al. 2007). Particles <63 μm (i.e., fines) consisting of silt and clay have a high surface area and are more likely to absorb heavy metals because of their surface chemistry. The percent of fines was 87.80–98.66 % of the sediments (Supplementary Table S3), indicating that the studied sediments in the TGR were primarily composed of silt and clay.

The WQC are also important in calculating SQGs. WQC determined by hardness (CaCO<sub>3</sub>, mg/L) and the Chinese Grade I and Grade II WQC are shown in Table 3. WQC based on hardness were lower in the mainstream than in the three tributaries; the Yangtze River had the lowest hardness of 52.03 mg/L (Supplementary Table S4). In the three tributaries, the river mouth area had relatively higher hardness. In general, the WQC based on hardness were significantly different from the Chinese Grade I and Grade II WQC. The WQC for Cu and Pb based on hardness were lower than the Chinese Grade I WQC. For Cd and Zn, the WQC were between Grade I and Grade II. The WQC for Ni could not be compared because of the lack of a WQC for Ni in China. These differences may arise from the geochemical properties of different regions (Fang and Xu 2007).

**Table 2** Correlation results for variables influencing SQGs

Sampling site	Cu			Cd			Pb			Zn			Ni							
	$K_p$	$WQC_i$	$M_{AVSi}$	$M_{Ri}$	$K_p$	$WQC_i$	$M_{AVSi}$	$M_{Ri}$	$K_p$	$WQC_i$	$M_{AVSi}$	$M_{Ri}$	$K_p$	$WQC_i$	$M_{AVSi}$	$M_{Ri}$				
ZY-1	3.35E+03	0.0076	0.2251	34.90	7.58E+03	0.0019	0.0071	0.12	1.07E+05	0.0020	0.70	11.16	3.67E+04	0.1004	0.67	100.39	3.17E+03	0.0442	0.1762	42.33
ZY-2	3.00E+03	0.0078	0.2013	23.48	2.90E+03	0.0020	0.0056	0.04	6.66E+04	0.0021	0.44	6.39	3.16E+04	0.1033	0.60	83.01	2.96E+03	0.0455	0.1876	36.95
ZY-3	3.80E+03	0.0092	0.2451	32.38	7.95E+03	0.0023	0.0090	0.29	1.18E+05	0.0026	0.83	11.54	5.05E+04	0.1213	0.76	89.49	3.43E+03	0.0534	0.1764	38.14
MX-1	3.11E+03	0.0054	0.1435	20.52	4.23E+03	0.0014	0.0027	0.04	3.32E+04	0.0013	0.39	9.02	1.70E+04	0.0714	0.52	81.80	2.36E+03	0.0315	0.1762	35.23
MX-2	1.73E+03	0.0052	0.2320	20.89	8.01E+03	0.0014	0.0056	0.07	4.72E+04	0.0012	0.48	4.22	2.54E+04	0.0687	0.71	76.60	3.36E+03	0.0303	0.2442	37.34
MX-3	3.06E+03	0.0051	0.1086	23.21	4.17E+03	0.0014	0.0024	0.06	5.11E+04	0.0012	0.27	6.40	2.21E+04	0.0675	0.36	79.29	2.05E+03	0.0297	0.1175	37.08
MX-4	5.51E+03	0.0063	0.1300	17.76	4.69E+03	0.0016	0.0042	0.55	6.81E+04	0.0016	0.40	13.72	3.49E+04	0.0827	0.41	123.78	4.13E+03	0.0364	0.0955	38.87
MX-5	4.39E+03	0.0069	0.3339	31.51	6.20E+03	0.0018	0.0107	0.16	1.24E+05	0.0018	1.02	9.35	4.94E+04	0.0912	1.05	81.54	2.97E+03	0.0401	0.2452	39.03
CT-1	3.65E+03	0.0076	0.0213	19.73	3.43E+03	0.0019	0.0005	0.08	1.81E+04	0.0020	0.05	5.75	2.49E+04	0.0998	0.06	76.81	2.80E+03	0.0439	0.0205	34.93
CT-2	4.67E+03	0.0074	0.1315	30.21	5.50E+03	0.0019	0.0051	0.18	8.40E+04	0.0020	0.34	8.54	3.35E+04	0.0973	0.35	94.48	2.58E+03	0.0429	0.1033	41.64
CT-3	5.05E+03	0.0097	0.1905	30.11	6.72E+03	0.0024	0.0061	0.21	1.72E+05	0.0028	0.62	8.88	3.50E+04	0.1282	0.64	88.59	2.25E+03	0.0564	0.1442	39.18
Yangtze	7.50E+03	0.0051	0.5262	34.10	5.96E+03	0.0014	0.0067	0.12	1.53E+05	0.0012	1.18	8.52	5.94E+04	0.0679	0.93	82.05	4.57E+03	0.0299	0.2610	40.37

Units: WQC, mg/L;  $M_{AVSi}$ , mg/kg;  $M_{Ri}$ , mg/kg

**Table 3** USEPA water quality criteria based on hardness and comparison with freshwater quality standards in China (mg/L) (USEPA 2009; SEPAC 2002)

Sampling site	Cu	Cd	Pb	Zn	Ni
ZY	0.0082	0.0021	0.0023	0.1083	0.0477
MX	0.0058	0.0019	0.0020	0.0987	0.0434
CT	0.0082	0.0017	0.0017	0.0871	0.0384
Yangtze	0.0051	0.0014	0.0012	0.0679	0.0299
Grade I	0.01	0.001	0.01	0.05	–
Grade II	1	0.005	0.01	1	–

Hyphen (–) means lack of related quality standards in China

Residual heavy metals ( $M_{Ri}$ ) are present in chemically stable mineral forms or bound to non-labile soil fractions. They are less mobile and bioavailable and, hence, less toxic (Zhang et al. 2010).  $M_{Ri}$  is also significant in calculating the SQGs. The proportion of residual metals varied for different metals (Supplementary Fig. S1). The mean proportion of  $M_{Ri}$  for Cu, Cd, Pb, Zn, and Ni was 47.66, 16.00, 18.55, 54.78, and 76.53 %, respectively (Supplementary Fig. S1).

Heavy metals in the sediments that combine with AVS are expected to have minimal bioavailability (Li et al. 2014a). Therefore, in the modified EqP approach,  $M_{AVSi}$  are also components of calculating the SQGs. Very low  $M_{AVSi}$  were measured for all sediments (Table 2), because sediments in the TGR are primarily oxidized (Fang and Xu 2007).

Proportions of the metals in each of these forms are shown in Supplementary Fig S2. For Cu,  $K_p \times WQC_i$ ,  $M_{AVSi}$ , and  $M_{Ri}$  ranged over 29.85–65.80, 0.0450–0.1107, and 33.94–69.38% with mean values of 49.88, 0.3824, and 49.73 %, respectively. For Ni, the proportions of  $K_p \times WQC_i$  were higher than for Cu (62.08–82.71 %, mean 74.92 %), and  $M_{AVSi}$  and  $M_{Ri}$  were lower (0.0130–0.1755 and 17.21–37.80 %, means 0.1051 and 24.97 %, respectively). Cd, Pb, and Ni had similar distributions with  $K_p \times WQC_i$  accounting for 82.22–99.36 %; the percentages of  $M_{AVSi}$  and  $M_{Ri}$  were 0.0024–0.76418 and 0.6167–17.05 %, respectively. On the whole, different components (i.e., binding phases) made different contributions to the SQGs.  $K_p$ , WQC, and  $M_R$  were the predominant factors affecting the SQGs.  $M_{AVSi}$  accounted for only 0.0024–0.7707 % of the metals in sediments. Therefore, under strongly oxidative conditions, the effect of AVS on the SQGs can be neglected.

### Sediment quality guidelines for the Three Gorges Reservoir

We calculated SQGs for the TGR using the EqP approach recommended by USEPA (Table 4). The SQGs for Zn were 1–2 orders of magnitude higher than for the other elements. We also used the Chinese Grade I and Grade II WQC to

**Table 4** Comparison of Yangtze River SQGs with other available SQGs (mg/kg)

Sediment quality guidelines	Cu	Cd	Pb	Zn	Ni	Reference
ZY <sup>a</sup>	58.45	13.06	232.64	4448.87	191.94	
ZY <sup>b</sup>	64.33	6.30	983.22	2071.49	–	
ZY <sup>c</sup>	3415.81	30.88	983.22	39688.76	–	
MX <sup>a</sup>	44.17	10.16	173.29	3620.79	167.69	
MX <sup>b</sup>	58.72	5.16	735.11	1737.99	–	
MX <sup>c</sup>	3331.63	25.27	735.11	33137.31	–	Present study
CT <sup>a</sup>	63.85	11.97	145.17	3112.27	156.82	
CT <sup>b</sup>	53.63	6.87	669.61	1632.42	–	
CT <sup>c</sup>	2907.35	33.80	669.61	31065.83	–	
Yangtze <sup>a</sup>	73.05	8.35	197.41	4120.12	177.49	
Yangtze <sup>b</sup>	109.62	6.09	1539.15	3055.30	–	
Yangtze <sup>c</sup>	7533.90	29.94	1539.15	59529.43	–	
ISQG <sub>low</sub>	65	1.5	50	200	21.00	McCready et al. (2006)
ISQG <sub>high</sub>	270	10	220	410	52.00	
TEC	31.6	0.99	35.8	121	22.7	MacDonald et al. (2000)
PEC	149	4.98	128	459	48.6	
ISQV <sub>low</sub>	65	1.5	75	200	40.00	Chapman et al. (1999)
ISQV <sub>high</sub>	270	9.6	218	410	–	
Yangtze River mouth	25	2	12	109	–	Huo and Chen (1997)
Middle-lower reaches of Yangtze River	650	1.7	250	300	–	Wang (1994)
Yangtze river mouth	13	0.01	7	62	–	
Stem stream of the Yangtze River	783–994	43.3–54.1	6.7–91	783–944	2110–2690	
Yangtze River water system	54.1–610	2.74–167	5.5–601	412–9890	143–12900	Fang and Xu (2007)

<sup>a</sup> USEPA water quality criteria

<sup>b</sup> SEPAC national Grade I surface water quality criteria

<sup>c</sup> SEPAC national Grade II surface water quality criteria

ISQG interim sediment quality guideline, ISQV interim sediment quality value, PEC probable effects concentration, TEC threshold effects concentration

calculate SQGs; however, Ni was not included because of the absence of a Chinese WQC. The SQGs were closely related to the WQC. The SQGs based on Grade I WQC for Cd and Pb at all sampling sites and Cu in the Caotang River were all lower than the values based on hardness. The SQGs based on the Grade II WQC all exceeded the criteria based on hardness.

ISQG<sub>low</sub>/ISQG<sub>high</sub>, TEC/PEC, and ISQV<sub>low</sub>/ISQV<sub>high</sub> are internationally used SQGs developed based on empirical relationships between heavy metal concentrations in freshwater sediments and toxic effects. The SQGs for Cd, Pb, Zn, and Ni we developed were all an order of magnitude higher than the ISQG<sub>low</sub>/ISQV<sub>low</sub> and somewhat higher than the ISQG<sub>high</sub>/ISQV<sub>high</sub>. However, the SQGs for Cu we established were lower than the ISQG<sub>low</sub> and ISQV<sub>low</sub> except for the Yangtze River and were between the most rigorous standards TEC and PEC (Table 4). These differences may be attributed to the derivation method, level of protection, screening of key environmental factors, and the characteristics of the sediments (TOC, AVS, and pH) (Chen et al. 2005), all of which increase the complexity of SQG development and use.

Previous studies providing SQGs for the Yangtze River are also listed in Table 4. The SQGs for Pb and Zn we developed were near the upper end of the range of previous values. This may be attributed to the high  $K_p$  values and percent fines in the present study. The TGR slows the flow rates of the rivers, increasing sediment stability. Heavy metals adsorb onto the fine particles and are deposited on the bottom of the TGR, resulting in the relatively high SQGs. For Cu and Cd, the results were about the same order of magnitude as in previous studies. Studies of Ni in China are rare because of the absence of WQC; previously reported SQGs ranged widely over 143–12,900 mg/kg. In general, previously developed SQGs in China have been fairly rough estimates. The existing WQC for China may not represent the WQC that would be appropriate for a specific area, although they are good reference values. Similarly, the EqP model better reflects the actual conditions compared to empirical SQGs. Remaining inaccuracies may be attributed to other uncertainties in the SQGs; for example, a large variety of contaminants are present in sediments that may interact with each other. The SQGs we

established were higher than the total concentrations of heavy metals (Supplementary Table S5), demonstrating that heavy metals have no potential risk to aquatic organisms except for Cu, whose concentrations were slightly larger than the SQGs in some areas.

## Conclusions

The EqP model was used to assess heavy metal toxicity and establish SQGs for the TGR. The results indicate that the surface sediments in the TGR were oxic or suboxic. Sediments with  $[SEM] - [AVS] > 0$  might have no biological toxicity based on  $([SEM] - [AVS])/f_{oc}$ ;  $[SEM] - [AVS]$  overestimated the heavy metal toxicity in the TGR. In this study,  $K_p$ , WQC, and  $M_R$  were the main factors affecting the SQGs, while  $M_{AVS}$  could be neglected. The SQGs we established provide a scientific basis for further evaluation of heavy metal toxicity in the TGR. Although the EqP approach has been supported by a number of sediment toxicity tests in deriving SQGs, AVS and TOC used in this study provide a useful tool to improve the reliability of SQGs; the application of this approach was also confounded by the various components that ameliorate the bioavailability of metals. Therefore, much additional research is needed to improve the reliability of SQGs such as considering the influence of particle size and other factors.

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