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Species sensitivity analysis of heavy metals to freshwater organisms

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Abstract Acute toxicity data of six heavy metals [Cu, Hg, Cd, Cr(VI), Pb, Zn] to aquatic organisms were collected and screened. Species sensitivity distributions (SSD) curves of vertebrate and invertebrate were constructed by log–logistic model separately. The comprehensive comparisons of the sensitivities of different trophic species to six typical heavy metals were performed. The results indicated invertebrate taxa to each heavy metal exhibited higher sensitivity than vertebrates. However, with respect to the same taxa species, Cu had the most adverse effect on vertebrate, followed by Hg, Cd, Zn and Cr. When datasets from all species were included, Cu and Hg were still more toxic than the others. In particular, the toxicities of Pb to vertebrate and fish were complicated as the SSD curves of Pb intersected with those of other heavy metals, while the SSD curves of Pb constructed by total species no longer crossed with others. The hazardous concentrations for 5 % of the species (HC_5) affected were derived to determine the concentration protecting 95 % of species. The HC_5 values of the six heavy metals were in the descending order: Zn > Pb > Cr > Cd > Hg > Cu, indicating toxicities in opposite order. Moreover, potential affected fractions were calculated to assess the ecological risks of different heavy metals at certain concentrations of the selected heavy metals. Evaluations of sensitivities of the species at various trophic levels and toxicity analysis of heavy metals are necessary prior to derivation of water quality criteria and the further environmental protection.

Keywords Heavy metals · Aquatic organisms · Species sensitivity distributions (SSD) · Ecological risks · Toxicity

Introduction

Widespread pollution from heavy metals is one of the major causes of the poor freshwater quality currently observed globally (Liu et al. 2009; Montuori et al. 2013; Sekabira et al. 2010). Human activities such as industrial effluent, agricultural drainages, vehicle emissions and domestic wastes have all posed serious risks associated with heavy metals exposure to human and water bodies (Adnano 1986; Moore and Ramanamoorthy 1984; Sekhar et al. 2003; Green et al. 2010). For example, some heavy metals such as Zn and Cu are essential for the growth and well-being of living organisms including human beings. Other elements such as Hg and Cr are not essential for metabolic activities and exhibit toxic to aquatic organism.

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Cd and Cr have been reported to be the cause of several serious pollution incidents recently in China (Burchard-Levine et al. 2012; Lin et al. 2005; Gao and Xia 2011). However, the presence of heavy metals in ecosystems becomes dangerous for organisms when the concentration rises above the natural background in water (Lopa and Adhikari 2006). Unlike other pollutants, heavy metals have been paid more attentions because they are persistent, non-degradable, toxic, and can be bioconcentrated and biomagnified, which can transfer to the human body via food chain and pose serious threats to the environment (Gavrilescu 2004; Lai et al. 2005; Townsend et al. 2013). As a particular pollutant may produce different detrimental effects in various organisms (Maltby et al. 2005), there is an increasing need to evaluate the risks that the heavy metals may pose to different aquatic organisms.

Freshwater species consist of vertebrates and invertebrates. A diverse range of fish, reptiles, and amphibians make up vertebrates, and invertebrates mainly consist of crustaceans, mollusk and worms. Fish and cladoceran are dominant vertebrates and invertebrates, respectively. Previous studies have revealed that the toxicity mechanism of heavy metals to species at various trophic levels are different (Amiard et al. 2006). Sensitive test organisms screening is a crucial prerequisite for water quality criteria (WQC) derivation, and there has been some related researches (Wang et al. 2014a, b, c; Zheng et al. 2014; Cai et al. 2014). *Daphnia magna* for invertebrates, *Danio rerio* for fish are standard test organisms. While the sensitivity of these standard test organisms to different pollutants differ a lot, *D. magna* is not always the most sensitive species such as it shows much lower sensitivity to neonicotinoids compared to insects (Rubach et al. 2010). The study aims to better understand taxonomic differences in species sensitivity.

The species sensitivity distribution (SSD) analysis is based on cumulative probability distributions of toxicity values for multiple species. The SSDs represent the variation in sensitivity of species toward a contaminant by a statistical or empirical distribution function of responses for a set of species (Posthuma et al. 2002). This method was first proposed by Kooijman (1987) and later improved by subsequent studies (Aldenberg and Slob 1993; Newman et al. 2000; Posthuma et al. 2002; Wagner and Løkke 1991). SSD method has been widely used to assess the ecological risks posed by heavy metals (Hall et al. 1998; Brix et al. 2001; Van Sprang et al. 2004). SSD is also used to calculate the concentration at which a specified proportion of species will be affected, referred to as the hazardous concentration (HC) for *p* (%) of species (HCp) (Newman et al. 2000). The most frequently estimated HCs are the HC_5, the concentration by which protecting 95 % of species not affected (US EPA 2004; Dyer et al. 2006). Meanwhile, the percentile of species associated with a certain concentration can be used to assess the toxicity of a specific heavy metal and also the potential affected species.

Numerous studies have addressed the direct impacts of heavy metals on freshwater organisms (Priel and Hershfinkel 2006; Birungi et al. 2007). However, studies on comparisons of toxicity different heavy metals are relatively limited, while mostly using only one or a few substances and species (Li et al. 2012; Zhang et al. 2014). Therefore, this study aimed to reveal the relationship between the species sensitivity of taxonomic diversity and the toxicity of heavy metals. Six heavy metals, including copper (Cu), mercury (Hg), cadmium (Cd), hexavalent chromium [Cr(VI)], lead (Pb) and zinc (Zn) were selected to assess the toxic effects of heavy metals on various taxa species and compare the sensitivities of different taxa species to each heavy metal. Based on the toxicological data of heavy metals for native species in China, SSD curves were constructed individually for different taxonomic groups by a log-logistic model. In addition, an attempt was made to rank sensitivities of different taxa species exposed to a given heavy metal. Moreover, comprehensive comparison of SSD in different trophic levels was performed to assess ecological risks of six typical heavy metals to aquatic organisms.

Materials and methods

Ecotoxicity data collection and screening

Ecotoxicity data of six heavy metals, namely Hg, Cu, Cr(VI), Cd, Pb and Zn were collected from the ECOTOX database (http://cfpub.epa.gov/ecotox/), CNKI (www.cnki.net) and various publications (e.g., research papers). The selected key words in the search include "mercury", "copper", "chromium", "cadmium", "lead", "zinc", "heavy metals", "ecotoxicity", etc.

The data from literatures were screened according to the following screening criteria (Stephan et al. 1985): acute toxicity data indicators of LC_{50} and EC_{50}; the exposure time of 48 h for *Daphnia* and *Chironomid larve*, and 96 h for other aquatic animals; chronic toxicity data were excluded because of insufficiency; the toxicity data of a certain species in its sensitive life stages when data of multiple life stages were available. If toxicity data for one species vary a lot (>10 times), outliers should be discarded; physicochemical parameters (e.g., temperature, oxygen, and particulate matter concentration) should be carefully controlled during the experiment; experimental substance concentrations must be measured at the beginning and the end of the experiment, and the actual concentrations should not deviate from the nominal concentrations by more than

20 %. Also, the qualified data should be processed according to scientific test principles, including design of control group, conduction of quality control, etc.

Data analysis

When more than one toxicological data were obtained for one species, the geometric mean value (species mean acute value, SMAV) was calculated and used as the estimate for this species. The SMAVs were used as the modeled effect metrics and fitted to the SSD (Van Vlaardingen and Verbruggen 2007), and the species sensitivity was analyzed subsequently. Many cumulative distribution functions have been used to fit SSDs (Erickson and Stephan 1988; Wagner and Løkke 1991; Aldenberg and Jaworska 2000; Van der Hoeven 2001; Chen 2004; Hose and Van den Brink 2004). In this study, in order to make the comparisons feasible and statistically meaningful, only the log–logistic distribution was used since it often fits the toxicity data well (Kooijman 1987; Newman et al. 2000; Wheeler et al. 2002; Versteeg et al. 1999) and provide more conservative HC_5s (Forbes and Calow 2002). The equation for the log–logistic model in this study is as follows:

$$y = 1/(1 + \exp((P1 - x)/P2))$$

where y is the cumulative probability of species, defined as (the order of the data point)/(1 + total number of data points), x is the mean of the log10-transformed LC_{50} or EC_{50} values, P1 is the parameter representing the intercept, and P2 is the parameter representing the slope of the curve. The distribution model was fitted to toxicity data points and evaluated using the χ^2 goodness-of-fittest with the adjusted coefficient of determination R^2 (Adj-R^2) in the software OriginLab 8.0 (USA, Origin Lab Company).

The SSDs for total species, invertebrates and vertebrates were compared using the two-sample Kolmogorov–Smirnov test and Mann–Whitney test in the SPSS software (SPSS 20.0 for Windows). Moreover, HC_5 and HC_{50} were calculated and compared between invertebrates and vertebrates taxa.

Results

Data collection and SSD construction

As shown in Table 1, a total quantity of 45, 54, 26, 26, 47, 30 aquatic species were collected for Cd, Cu, Pb, Zn, Hg, Cr(VI), respectively. The acute toxicity data sets for Cu, Cd and Hg were comparable in size, with smaller data sets for the other heavy metals. More than 50 % of vertebrates and invertebrates were from fish and cladoceran, respectively. To investigate the toxicity of six heavy metals on aquatic organisms at various trophic levels, SSD curves of invertebrates, cladoceran and vertebrates, fish were constructed and depicted in Fig. 1. The results indicated that the log–logistic distribution fits most of the taxa data points, with Adj-R2 of different taxa ranging from 0.89 to 0.99 ($p < 0.01$) (as shown in Table 1).

Table 1 Data quantity and goodness-of-fit of different taxonomic groups for six heavy metals

Heavy metals	Taxa group	Data quantity (*n*)	Adj-R^2	*p*
Cd	Total	45	0.98	<0.01
	Fish	12	0.92	<0.01
	Cladoceran	10	0.93	<0.01
	Vertebrate	16	0.95	<0.01
	Invertebrate	29	0.97	<0.01
Cu	Total	54	0.98	<0.01
	Fish	14	0.97	<0.01
	Cladoceran	19	0.99	<0.01
	Vertebrate	19	0.98	<0.01
	Invertebrate	35	0.96	<0.01
Pb	Total	26	0.97	<0.01
	Fish	11	0.92	<0.01
	Cladoceran	7	0.97	<0.01
	Vertebrate	11	0.92	<0.01
	Invertebrate	15	0.98	<0.01
Zn	Total	26	0.97	<0.01
	Fish	6	0.9	<0.01
	Cladoceran	13	0.96	<0.01
	Vertebrate	9	0.94	<0.01
	Invertebrate	17	0.98	<0.01
Hg	Total	47	0.97	<0.01
	Fish	15	0.95	<0.01
	Cladoceran	11	0.95	<0.01
	Vertebrate	22	0.97	<0.01
	Invertebrate	25	0.99	<0.01
Cr	Total	30	0.94	<0.01
	Fish	9	0.94	<0.01
	Cladoceran	12	0.89	<0.01
	Vertebrate	13	0.98	<0.01
	Invertebrate	17	0.94	<0.01

p is the significance level of the adjusted coefficient of determination (R^2)

For the five heavy metals except Hg, invertebrates were largely susceptible than vertebrates and the concentrations posing risk to most sensitive species differed by a range from one to three orders of magnitude, 63.8 μg L^{-1} for *Ceriodaphnia dubia* to Pb compared with 170 μg L^{-1} for *Cyprinus carpio* at a minimum and 3 μg L^{-1} for *Diaphanosoma brachyurum* to Cr(VI) compared with 10,700 μg L^{-1} for *Aristichthys nobilis* at a maximum As to Hg, *Ictalurus*

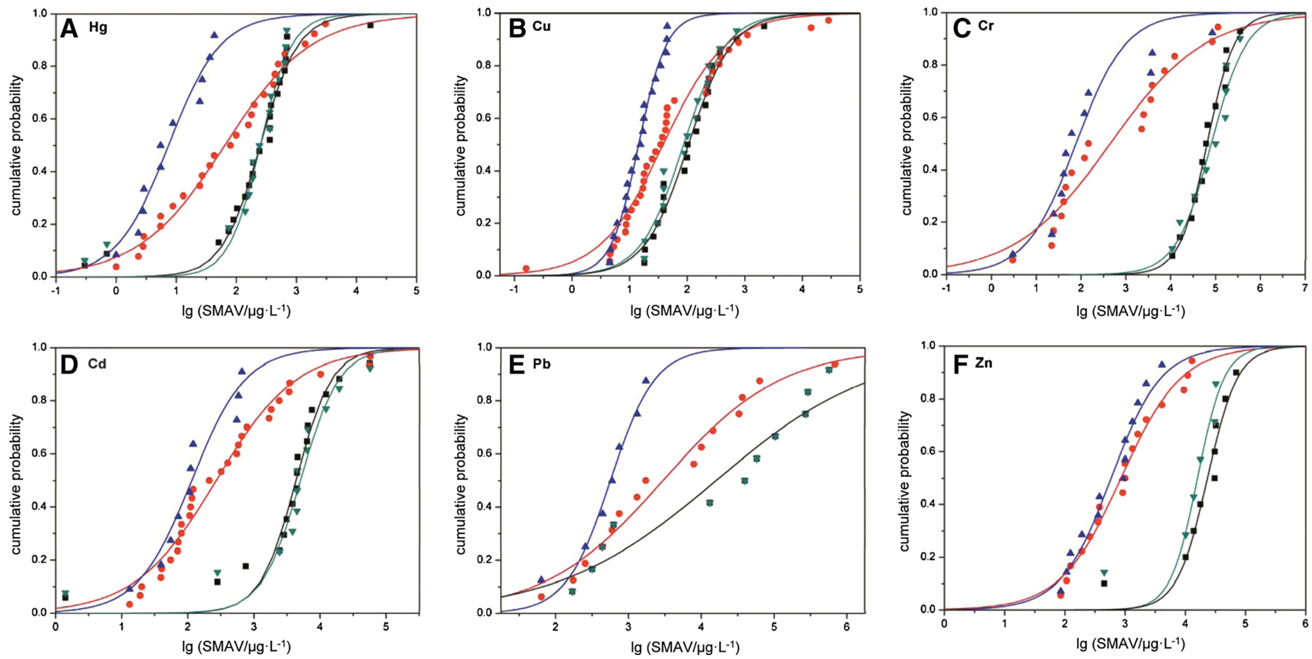

Fig. 1 Species sensitivity distribution of different taxonomic groups species for Cd, Cu, Pb, Zn, Hg and Cr(VI), *triangle* stands for cladoceran, *circle* for invertebrates, *rectangle* for vertebrates and *inverted triangle* for fish

punctatus with the concentration of 0.3 μg L^{-1} and *Carassius auratus* with 0.7 μg L^{-1} were both more sensitive than the most sensitive invertebrate *Moina macrocopa* with 1 μg L^{-1}. Furthermore, the most sensitive fishes also ranked first among vertebrates and the most sensitive cladoceran was also most vulnerable among invertebrates except for Cu, to which the most sensitive *Tubifex tubifex* belonged to annelid instead of cladoceran.

Species sensitivity of different taxa groups to heavy metals

The SSDs of a particular heavy metal constructed for each group were compared to assess the sensitivity of diverse trophic levels (Fig. 1). Overall, all heavy metals might have similar modes of toxic action for invertebrates and vertebrates, because the SSD curves of invertebrate species were shifted left from those of vertebrate to each heavy metal, indicating the invertebrate species was more susceptible than vertebrate. The sensitivities differed by a range from one to three orders of magnitude, and only invertebrates were slight higher than vertebrates for Cu. It is noteworthy that crossing situations existed between the SSD curves of invertebrates and vertebrates. For example, the SSDs of invertebrate and vertebrate crossed at higher concentration such as Cu and Cr(VI); vertebrate was more sensitive to Hg exceeding a certain high concentration, and the crossing happened at lower concentration for Pb. Moreover, it was obvious that fish was more resistant to the selected heavy metals than cladoceran except for Pb. The analysis of the significance level was performed and showed in Table 2. In most of the cases, p values were smaller than 0.05, indicating significant difference between distributions except for Hg and Pb.

The concentrations corresponding to 5 and 50 % of the affected species in the SSD curves of each community should be paid special attention because the former ascertain the safety of most species below the corresponding concentration and the latter means the majority of species are endangered. Thus, HC_5 and HC_{50} were calculated based on the SSD curves for six heavy metals and summarized in Table 3. In general, the HC_5 derived from invertebrates for each heavy metal was all lower than vertebrates with several orders of magnitude except for Pb (the HC_5 of invertebrates and vertebrates were closed to each other). The results demonstrated that the adverse effects of each heavy metal on invertebrate species were considerably bigger than on vertebrate. In other words, more invertebrates were affected at the same concentration than vertebrates. In addition, invertebrates were more sensitive than cladoceran to most of the selected heavy metals except slightly less to Hg. However, HC_5 values for invertebrate were lower than other taxa groups indicating more sensitivity except to Pb. Overall, HC_5 of different taxonomic groups showed a descending order of vertebrate > fish > cladoceran > invertebrate, indicating that invertebrate species were more sensitive than species of other taxonomic groups. The maximum HC_5 values varied from 9 times to more than 20,000 times compared with the minimum. However, the general order was found to be inconsistent for a gradient of increasing concentrations. For example, the HC_{50} values of cladoceran were as all ahead of invertebrate, and vertebrate were more sensitive higher than fish for Cd and Cr. Therefore, the sensitivity of different taxonomic groups and the toxic mode of action of toxicants should be taken into account for the ecological risks assessment of heavy metals.

Table 2 Comparison of species sensitivities to heavy metals for different taxa groups

Heavy metals	Taxa groups	ks	*p* (K–S test)	*p* (M–W test)
Cd	Invertebrate	0.64	0	0.001
	Vertebrate			
	Fish	0.833	0.001	0.001
	Cladoceran			
Cu	Invertebrate	0.4	0.039	0.066
	Vertebrate			
	Fish	0.684	0.001	0
	Cladoceran			
Pb	Invertebrate	0.412	0.231	0.281
	Vertebrate			
	Fish	0.636	0.063	0.085
	Cladoceran			
Zn	Invertebrate	0.778	0.002	0
	Vertebrate			
	Fish	0.833	0.007	0.003
	Cladoceran			
Hg	Invertebrate	0.389	0.058	0.092
	Vertebrate			
	Fish	0.867	0	0.001
	Cladoceran			
Cr	Invertebrate	0.824	0	0
	Vertebrate			
	Fish	0.917	0	0
	Cladoceran			

ks is a test statistic parameter used to indicate the significance level; *p* represents the significance level, $p > 0.05$ means the difference between distributions is not significant

Comparison of toxicity of the six heavy metals against the same taxa group

From the viewpoint of a certain trophic species, the SSD curves of six heavy metals against the same taxa group were gathered and also compared. As shown in Fig. 2a, b, generally, the curves of Cu and Hg were shifted left from others and the curves of Cd and Zn distributed in the middle and Cr on the right. In particular, the SSD curves of Pb intersected with those of other heavy metals, with crossing the curves for Cu and Hg at the cumulative probability of <0.10 (HC_{10}), crossing the curve of Cd at about 0.30 (HC_{30}), and that of Zn and Cr(VI) at above HC_{50} successively. Especially at the lower concentration, the curves of Pb were shifted left from that of Cu, indicating more vertebrates or fish being threatened. The copper is the most toxic to vertebrate among the six selected heavy metals, with the HC_5 calculated at 8.06 $\mu g\ L^{-1}$ for HC_5, followed by Hg, Cd, Zn, Cr(VI) in order. The HC_5 value of Cr(VI) were found to be more than 100 times higher than that of Cu. When the concentration of heavy metals was below 10 $\mu g\ L^{-1}$ vertebrate and fish were more affected by Pb even than exposure to Hg and Cu. When the concentration of Cd rose up to 100 $\mu g\ L^{-1}$, vertebrate and fish were not affected; but with the concentration up to 1000 $\mu g\ L^{-1}$, the sensitivity of the two increased rapidly. The HC_5 and HC_{50} values of Pb ranked the second and the fourth respectively, and HC_{50} was about four times compared with the third Cd, showing less toxic. The sensitivity (Table 2; Fig. 2b) followed in descend order (HC_5: Cu > Pb > Hg > Cd > Zn > Cr, HC_{50}: Cu > Hg > Cd > Pb > Zn > Cr).

For invertebrate, most of curves crossed, especially in lower concentration, indicating the sensitivities below and

Table 3 The calculated HC_5 and HC_{50} values of vertebrate, fish, invertebrate, cladoceran and total species for six heavy metals

	Heavy metals	Cu ($\mu g\ L^{-1}$)	Hg ($\mu g\ L^{-1}$)	Cd ($\mu g\ L^{-1}$)	Cr ($\mu g\ L^{-1}$)	Zn ($\mu g\ L^{-1}$)	Pb ($\mu g\ L^{-1}$)
HC_5	Total species	1.82	3.52	5.34	5.58	23.1	10.3
	Vertebrate	8.06	75.2	695	8014	4251	10.0
	Fish	6.92	42.3	698	1997	3492	10.0
	Invertebrate	0.940	0.49	4.26	0.350	28.3	12.1
	Cladoceran	2.80	0.39	7.19	1.78	346	71.6
HC_{50}	Total species	57.9	140	760	6337	2507	5814
	Vertebrate	105	251	4304	63,794	23,339	16,082
	Fish	86.6	250	5008	79,122	15,913	16,082
	Invertebrate	38.2	64.5	268	444	853	3002
	Cladoceran	14.4	7.43	114	76.5	585	569

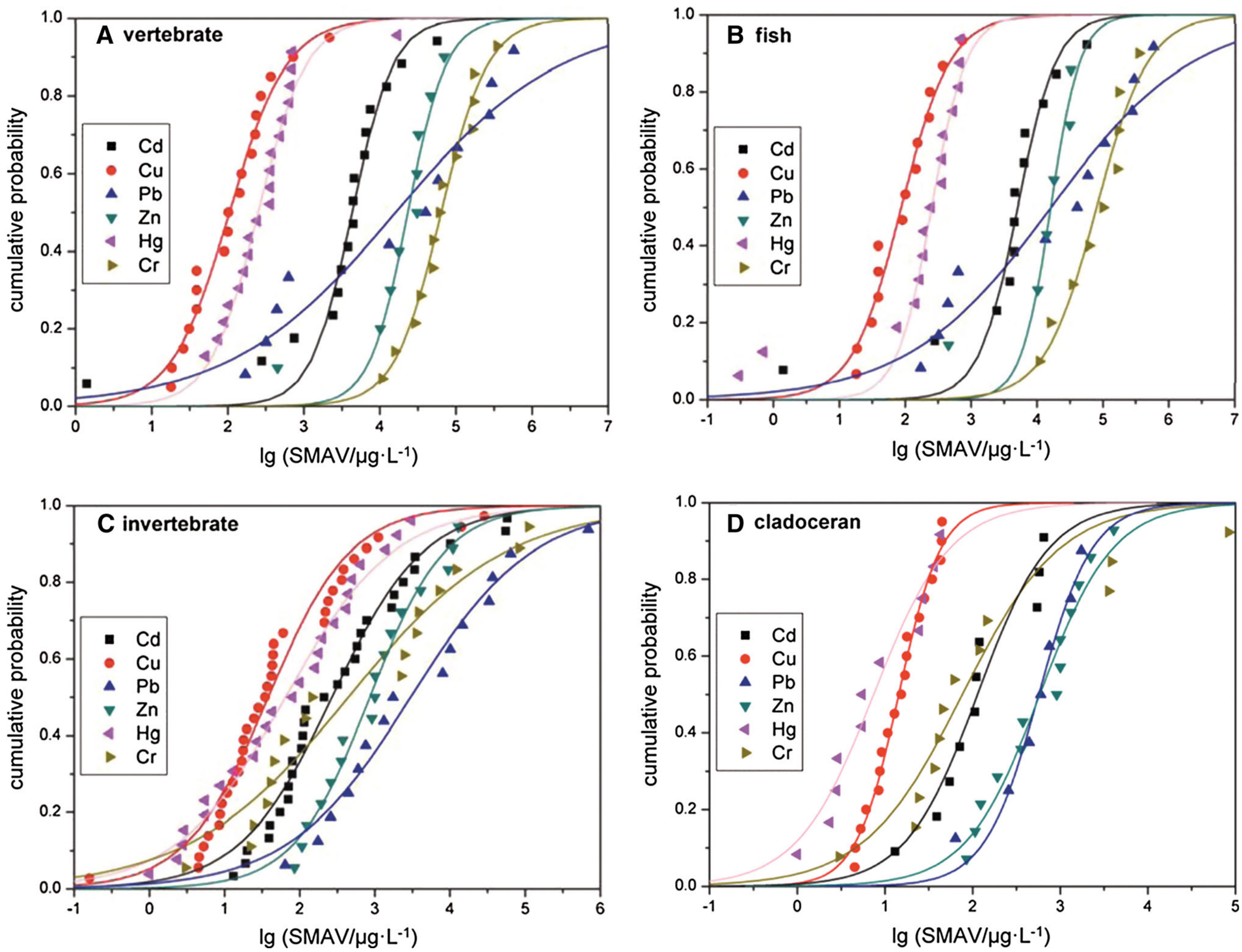

Fig. 2 SSD curves for vertebrates, fish, invertebrates and cladoceran exposed to different heavy metals

above intersecting points followed different trends. For example, the SSD curve of Cr(VI) at lower concentration was shifted to the left of that of Hg and Cu which indicating the invertebrate was most sensitive to Cr(VI). Interestingly, the phenomenon of obviously crossing for Pb to vertebrates disappeared. The toxicity of Pb on invertebrate was found to be less than that of Zn even at higher concentration. Instead of Pb, the SSD curves of Cr(VI) intersected with that of Cu and Hg below 0.20 (HC_{20}), that of Cd at about 0.40 (HC_{40}), that of Zn above HC_{60} successively. When the concentration of Cr(VI) was below 1 μg L^{-1} more invertebrate and cladoceran were affected even than exposure to Hg and Cu. When concentration of Cd was below 1 μg L^{-1}, invertebrate and cladoceran were not affected, but when the concentration reached up to 10 μg L^{-1}, the two taxa groups became increasingly sensitive. With respect to invertebrate, the toxicity of each heavy metal was generally higher, with HC_5 values all lower than 30 μg L^{-1}. HC_{50} values were mostly lower than 1 mg L^{-1} except those of Pb. For cladoceran, the HC_5 and HC_{50} values followed similar trends (HC_5: Hg > Cr > Cu > Cd > Pb > Zn, HC_{50}: Hg > Cu > Cr > Cd > Pb > Zn).

Comparison of SSDs of six heavy metals for total species

As shown in Fig. 3, SSDs of six heavy metals based on the total species were constructed and the relationship of sensitivity between individual taxa species and total species was investigated for all heavy metals. Interestingly, the phenomenon of obviously crossing for Pb and Cr(VI) for individual group disappeared. The adverse effect of Cd was in the middle among all heavy metals. Besides, the curves of Zn shifted on the left of Cr and Pb at higher concentration, and the toxicity of Zn was largely higher. The acute HC_5 values were respectively determined to be 1.82 μg L^{-1} for Cu, 3.52 μg L^{-1} for Hg, 5.34 μg L^{-1} for

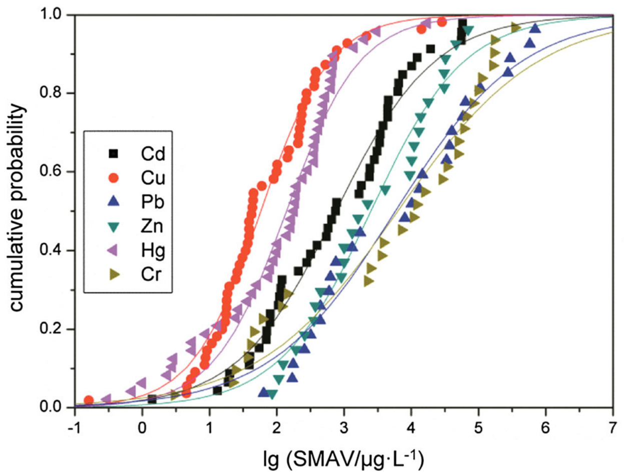

Fig. 3 SSD curves for total species exposed to different heavy metals

Cd, 5.58 μg L^{-1} for Cr(VI), 10.27 μg L^{-1} for Pb and 23.13 μg L^{-1} for Zn. These results manifested that all six heavy metals were highly poisonous to freshwater organisms. The sensitivity of total species to these heavy metals followed the order of: Cu > Hg > Cd > Cr > Zn > Pb for HC_5, Cu > Hg > Cd > Zn > Cr > Pb for HC_{50}. When the concentration was below 1 μg L^{-1}, there were no significant differences for the toxicities of Cu, Cd, Cr(VI), Zn and Pb, with Hg slightly more toxic. As the concentration increased to 10 μg L^{-1}, the ecological risks of Hg and Cu rose rapidly. In brief, the difference was not significant if the data of total species were all included.

The potential affected fractions of different groups at certain concentration

Potential affected fractions (PAFs) of the different trophic levels at certain concentration of the heavy metals reflect the degree of the lack of protection. As showed in Table 4, at 10 μg L^{-1}, 18.3 % of total species was affected by by Cu, 10.8 % by Hg, 27.8 % by Cd, 15 % by Cr, 22.4 % by Zn, and 4.9 % by Pb. At this concentration, 6.3 % of vertebrates was affected by Cu and 5 % by Pb, while Cd, Hg, Cr and Zn didn't pose ecological risks. The PAFs of fish were close to those of vertebrates. Therefore, when the concentration of heavy metals such as Hg and Cu came up to 10 μg L^{-1}, PAF of invertebrate (including cladoceran) varied from 24.5 to 57.4 %, which verified their high toxicity. When the concentration reached 1000 μg L^{-1}, 91.9, 82.8 and 63.4 % of total species were separately in the ecological risks of Cu, Hg and Zn, which indicated the three heavy metals were greatest toxicity. The adverse effects of Cr and Pb were not to be ignored as 45.2 and 30.6 % for PAF.

Discussion

According to the principle of SSD, both acute and chronic toxicology data can be used to construct SSD curves. Chronic toxicity data are more ecologically important because aquatic organisms are usually exposed to low concentrations of pollutants for a long time. Because chronic toxicity data are often insufficient and cannot meet the requirements of construction of SSD data for most pollutants (Wheeler et al. 2002; Hose and Van den Brink 2004). Acute data are more easily available to construct SSD curves instead of using chronic data during researches (Wang et al. 2008). Thus, in this study, only acute toxicity data were screened.

As the main components in SSD, the species composition and species sensitivity to chemicals could directly affect modeling of predictive values and accuracy of SSDs. The composition of species and sensitivities of organisms to chemicals in different ecosystems are related to their hydrographic geographic conditions (Brock et al. 2006). The species selected for constructing the SSD curves in this study were designed to represent examples that were naturally widely distributed in freshwater ecosystems of China. Consequently, the species sensitivity analysis of different categories are not only important when deriving WQC values but also a key issue when assessing the risk of water pollutants.

The result of comparing the sensitivity of different taxa groups showed that invertebrates appeared to be more sensitive than vertebrate to the six heavy metals selected. This may be because the skin of vertebrate (e.g., fish and amphibian) can isolate the chemicals and protect themselves from the toxic damage to some extent (Harri et al. 1979), while invertebrate like crustaceans and insects molt in their life-stages and would be more sensitive to chemicals just after molting (Hanazato 2001). Besides, the difference in sensitivity to these heavy metals may be attributed to the different patterns of exposure and accumulation in different organisms. The result was in compliance with the previous relevant study (Li et al. 2012).

The species evaluated herein showed sensitivity variations to different heavy metals treatments that were used in constructing the SSDs. The toxicity data of all heavy metals showed that the model organism *D. magna* was not the most sensitive species among the invertebrates, consistent with previous studies (Von der Ohe and Liess 2004; Wu et al. 2013). In particular, cumulative probability of *D. magna* exceeded 60 % in SSD curves of Cu, even higher than other cladocerans, suggesting caution should be taken when using surrogates. This also supported earlier conclusions that no species is consistently the most sensitive to chemicals over a wide range of modes of action (Mayer

Table 4 Predicted PAF values of the heavy metals under various concentrations

Heavy metals	Concentration/(μg L^{-1})	Total	Vertebrate	Fish	PAF invertebrate	Cladoceran
Cu	0.1	–			0.9	
	1	3.1	0.5	0.5	5.2	0.8
	10	18.3	6.3	7.5	25.6	34.2
	100	61.4	48.6	54.2	68.3	97.1
	1000	91.9	93	94.5	93.1	
Hg	0.1					1.2
	1	1.9			7.5	11.9
	10	10.8	1.15	0.5	24.5	57.4
	100	41.6	32.5	17.9	68.3	93.1
	1000	82.8	87.6	90.9	93.1	99.3
Cd	1	1.9				
	10	27.8			8.8	6.9
	100	23.1	0.2	0.29	33.3	93.1
	1000	54.1	8.7	8.3	71.9	91
	10,000	82.2	79.6	73.7	92.9	99.2
Cr	1	6.3			7.6	3.2
	10	15			17.4	16.9
	100	31.6			35.1	55.2
	1000	45.2	0	0.8	58.3	88.5
	10,000	76	6.7	9.3	78.3	97.8
	100,000	89.3	94.5	77.2	90.3	–
Zn	1				0.3	–
	10	22.4			2.1	1.4
	100	33.1			13.6	26
	1000	63.4	0.4	0.5	53.4	63.6
	10,000	70.5	18.8	20.3	89.3	95.1
	100,000	91	92.6	97.3	98	–
Pb	10	4.9	5	5	4.6	0.3
	100	11.7	11.7	11.7	14	7.8
	1000	30.6	24.8	24.8	35.8	56.1
	10,000	56.3	45.3	45.3	65.4	98.3
	100,000	78.9	67.5	67.5	86.7	–

and Ellersieck 1986). Statistical analysis also proved that invertebrates were more vulnerable than vertebrates and cladocera were more sensitive than fish, just as shown in Table 2. However, $p > 0.05$ from comparing invertebrates with vertebrates to Pb or Hg, which demonstrated that invertebrates were not more sensitive than vertebrates on the whole. As to Pb, the lack of sufficient species from varying trophic levels might have contributed to this result. The datasets were suggested to be no less than ten (Wheeler et al. 2002). In the present study, the dataset with large number of toxicity data was found to give better model fitting, as demonstrated by the best R^2 value being obtained for Cu among the six selected heavy metals.

SSD curves and HC_5 values are generally utilized to derive WQC for toxicants (Stephan et al. 1985; Wang et al. 2013, Wang et al. 2014a, b, c). The HC_5 is considered to be the concentration to protect 95 % test organisms according to the methodologies of development of WQC (US EPA 1985). The purpose of WQC is to protect more than 95 % of total species. So HC_5 can be used as a reference concentration to evaluate the toxicity of pollutants. HC_5 values, derived for the pollutants in this study for protecting Chinese species, differed from those published by the USEPA. Such difference was reasonable probably due to differences in geographical conditions and biota between two countries. Thus, the degree of protection desired for aquatic organisms should be formulated to fit local conditions. For those species with their cumulative probability below 0.05, they are out of protection even when the ambient concentration is lower than HC_5 value. In other word, these species should not be considered as indicators for risk assessment of corresponding heavy metal. It was worthy to be mentioned that HC_5 values of all heavy metals for total species showed significantly difference compared with HC_5 derived from each of four taxonomic groups. For example, HC_5 for total species was higher than that for vertebrate, fish and cladoceran, indicating several species belonging to invertebrate instead of cladoceran. In the fact, of the listed species not protected by the HC_5 for total species, only *Tubifex tubifex* belonging to annelid was in danger.

Greater attentions should be given to Hg and Cu that exhibited the greatest toxicities. Mercury was found to be the most toxic to cladoceran, belonging to arthropod, and *Moina macrocopa* was the most sensitive invertebrate to Hg and still unprotected when the exposure concentration is as low as HC_5 value. The results were in accordance with previous studies that show in the lower taxonomic classification level, the sensitivity of arthropod is more than that of fish in China (Li et al. 2012). In Figs. 2 and 3, Cu showed greater toxicity than most of other heavy metals, that might be because Cu is an essential metal to the normal physiology of crustaceans. On the contrary, Cd is generally not required for metabolic (Valavanidis and Vlachogianni 2010), and showed less toxicity than Cu and ranked in the middle of SSD in our study.

On the basis of the SSD curves of heavy metals in Fig. 2, the toxicity profiles were classified as highly toxic, moderately toxic, low toxic and lesser toxic within the whole concentration thresholds. Cr, Hg and Cu were classified as highly toxic metals on invertebrates, with HC_5 values between 0.35 and 0.94 $\mu g\ L^{-1}$. Cu and Hg were classified as moderately toxic metals on vertebrates (including fish), with HC_5 values between 6.92 and 10 $\mu g\ L^{-1}$, also Cd was classified as a moderately toxic metals on invertebrates with HC_5 values from 4.26 to 7.19 $\mu g\ L^{-1}$. Zn and Pb were classified as low toxic metals on invertebrates with HC_5 values from 12.05 to 345 $\mu g\ L^{-1}$. Zn and Cr were classified as lesser toxic metals on vertebrates with HC_5 values above 1000 $\mu g\ L^{-1}$. However, based on the HC_5 extrapolated by total species, Cu, Hg, Cd and Cr should be classified as moderately toxic from 1.82 to 5.58 $\mu g\ L^{-1}$, and Pb and Zn were classified as low toxic metals with 10.27 and 23.13 $\mu g\ L^{-1}$ for HC_5 values, respectively. So Cu was the most toxic heavy metal and indicated great ecological risk, although its human health toxicity is not that great. The difference in these classifications between different taxonomic groups would help to explain why SSD curves of Pb and Cr constructed for individual taxa group crossed that of other metals but this crossing didn't appear for the SSDs of total species.

In fact, PAF could partly reflect ecological risks of different heavy metals. When exposure concentration was 1 $\mu g\ L^{-1}$, the ecological risks of Cr and Hg was observed with PAF from 0.3 to 7.6 % among invertebrate. However, Cd, Cu and Hg, Zn, Cr(VI) exceeded the threshold of 10 % (PAF) at the exposure level of 10 $\mu g\ L^{-1}$. When exposure concentration came up to 1000 $\mu g\ L^{-1}$, most of aquatic organisms were affected by Cu and Hg.

However, the present study lays further emphasis on the facts that it is necessary to investigate the toxicity of heavy metals on taxa species from various trophic levels. Comprehensive comparisons demonstrated that the species sensitivity should be taken into consideration during the WQC derivation and risk assessment of each heavy metals. If not, over-protection or under-protection happened among taxa species under the WQC threshold of a given heavy metal. Therefore, evaluations of sensitivity of various trophic levels are necessary prior to derivation of WQC and the future development of water quality standard. As heavy metals contamination often happens in bay or coasts and poses a threat to the marine organisms, it is essential to evaluate the heavy metals risk and the sensitivities of marine organisms. The analysis of this study is positively correlated with the results from marine due to similar effect mechanisms of metals, providing a significant reference for marine WQC development and further marine environmental protection. Furthermore, more efforts should be put on the different sensitivity of taxa species to varying pollutants, not limited to typical heavy metals. Only in this way aquatic ecosystems can be protected by effective measures from governments.

Conclusions

The present study investigated the toxicity of six typical heavy metals towards vertebrate and invertebrate species. In general, sensitivities of invertebrate taxa to six heavy metals were higher than that of vertebrates. The ecological risks of all selected heavy metals to cladoceran were higher than to fishes. However, closer examination between vertebrate and invertebrate species dataset revealed consistent differences in the sensitivity of species to main heavy metals included, such that invertebrates were deemed to be more vulnerable. Species high ranking in the sensitivity to heavy metals are considered firstly in order to allocate more efforts towards relevant target species.

However, with respect to the same taxa species, the toxicities of six heavy metals were also assessed. Overall, Cu had the most adverse effect on vertebrates, followed by Hg, Cd, Zn and Cr. The toxicity of Pb should be paid attention because its SSD constructed by vertebrates crossing with the rest. When a comprehensive data set including vertebrates and invertebrates is available, Cu proved to be more prominent toxic than the other metals. The toxicities of the six heavy metals were listed in a descending order: Cu > Hg > Cd > Zn > Pb > Cr.

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Conflict of interest The authors declare that they have no conflict of interest.

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