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Development of Short-term Exposure Water Quality Standards for Cd, Cu, Pb and Zn in China

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Abstract

Environmental pollution sudden of heavy metals has posed serious ecological risks in China. However, local short-term exposure water quality standards (WQSs) are not yet established. In the present study, aquatic ecotoxicity data of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} to local species were collected and screened. The suitability of species sensitivity distribution (SSD) methods assumed to be used to derive the WQSs was evaluated by data analysis. Then, the methodology of short-term WQSs was established with the principles of SSD and ecological risk assessment, and the tiered short-term WQSs values of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} were derived with the established methodology. Finally, a case analysis was performed with the developed cadmium short-term WQSs and risk grades. The results may provide technical references for response to sudden environmental pollution.

Keywords: short-term exposure, water quality standard, sudden environmental pollution, ecological risk assessment, heavy metals

1. Introduction

Water quality standards (WQSs) play important roles in protection of ambient water environment quality. They can be divided into long-term exposure WQSs and short-term exposure WQSs. The latter meant to estimate severe effects and to protect most species against lethality during intermittent and transient events (e.g., spill events to aquatic-receiving environments, infrequent releases of short lived/ non persistent substances.). In contrast, long-term exposure guidelines are meant to protect against all negative effects during indefinite exposures (CCME, 2007). The technical system of long-term exposure WQSs have been established maturely in developed countries, such as the criterion continuous concentration (CCC) of the United States (USEPA, 1985), the water quality guidelines issued by the Canadian Council of Ministers of the Environment (CCME, 1991), the predicted no effect concentration of the European Union (ECB, 2003), the trigger values of Australia and New Zealand (ARMCANZ & ANZECC, 2000) and the negligible concentration (NC), the maximum permissible concentration (MPC), the serious risk concentration (SRC) issued by the Netherland (Traas, 2001).

The short-term exposure WQSs were studied earlier in the United States (US). In the American water quality criteria (WQC) document issued in 1968, also called “Green Book” (National Technical Advisory Committee to the Secretary of the Interior, 1968), the criterion maximum concentration (CMC) was proposed to deal with the acute exposure of pollutants, and the concept was still in use today in the US (USEPA, 2009). In recent years, many countries strengthen the study on the short-term exposure WQSs. Fox example, the Netherland issued the revised guidance for the derivation of environmental risk limits in 2007. In the guidance (van Vlaardingen and Verbruggen, 2007), in addition to the NC, MPC and SRC, a new concept of maximum acceptable concentration for ecosystem (MAC_{eco}) was proposed to protect the aquatic ecosystem against acute toxic effects exerted by exposure to short-term peak concentrations or against acute effects of transient exposure peaks.

The intense efforts were conducted to evaluate the acute toxicity of heavy metals on aquatic organisms (Redeker and Blust, 2004; Johnson et al., 2007; Priel and Hershfinkel, 2006; Birungi et al., 2007; Karntanut and Pascoe, 2002). Lots of acute toxicity data are available and the present CMCs were mainly derived from standardized acute toxicity data. Heavy metals such as Cd, Cu, Pb and Zn can damage freshwater organisms. For example, for zinc, the 96-h LC_{50} to invertebrate range from 0.1 mg/L to 14 mg/L and that of vertebrate range from 0.654 mg/L to 46.5

mg/L (Wu et al., 2011). Recently, Rachel, Andrew, Claudia, Pereira, and John (2014) ranked metals according to the threat they pose to freshwater organisms in the UK.

After decades of development, China has established relatively mature long-term exposure WQSs to protect the quality of surface water, ground water, marine water and so on. For instance, surface waters can be divided into five classes based on the surface water specific function classification and protection target, Class I and Class V belong to the most rigorous and the least rigorous WQS (GB3838-2002). However, short-term exposure WQSs are not yet developed, not even studied. On the other hand, at present, China has entered the period of high risk of pollution accident, and unexpected environment pollution events of various pollutants, especially heavy metals, occurred often. Fox example, recently, the serious sudden accident of cadmium pollution taking place in the Longjiang River in Guangxi Province has caused tens of tons of adult fish and more than one million fish fry death (Xinhua News Agency reported). The short-term exposure WQSs is needed urgently in China to assess the ecological risk posed by heavy metals in sudden pollution accidents. This study collected and screened the acute ecotoxicity data of Cd, Cu, Pb and Zn, and established the methodology of short-term WQSs with the principle of species sensitivity distribution (SSD) and ecological risk assessment. And, the tiered short-term exposure WQSs for the four heavy metals was derived. The results can provide valuable information to the environmental management of sudden pollution accident of heavy metals.

2. Method

The Method section describes in detail how the study was conducted, including conceptual and operational definitions of the variables used in the study, Different types of studies will rely on different methodologies; however, a complete description of the methods used enables the reader to evaluate the appropriateness of your methods and the reliability and the validity of your results, It also permits experienced investigators to replicate the study, If your manuscript is an update of an ongoing or earlier study and the method has been published in detail elsewhere, you may refer the reader to that source and simply give a brief synopsis of the method in this section.

2.1 Collection of Published Acute Ecotoxicity Data of Cd, Cu, Pb and Zn

The published acute toxicity data of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} to aquatic animals were collected from the ECOTOX database (http://cfpub.epa.gov/ecotox), TOXNET Database (http://toxnet.nlm.nih.gov), the China National Knowledge Infrastructure (www.cnki.net) and other open literatures. The data were screened according to the guidelines for deriving WQC for the protection of aquatic organisms in the US (USEPA, 1985). Unqualified data with unsuitable exposure time (for daphnia and midge, 2 days, and for other organisms, 4 days are suitable), unusual diluted water (such as distilled water), unscientific experimental design and relatively insensitive life stages were not selected. Data of non-Chinese species were also abandoned. As for the test endpoints, the 48 h-LC_{50} or EC_{50} for daphnia or larvae of midge, and 96 h-LC_{50} or EC_{50} for fish, mollusks, shrimp and other organisms were chosen.

2.2 Evaluation of the Suitability of Four SSD Methods

In order to obtain the optimal model, the suitability of several SSD methods assumed to be used to develop the methodology of short-term WQSs were evaluated. The hazardous concentrations for 5% of the species (HC_5) were calculated according to the four SSD methods that based on log-triangle (USEPA, 1985), log-normal (Van Vlaardingen, Traas, Wintersen, & Aldenberg, 2004), log-logistic (Aldenberg & Solb, 1993) and BurrIII function (Hose & Van den Brink, 2004), respectively. The model that gained a suitable HC_5 value was chosen to derive the pollutant concentration corresponding to different affected fractions of species.

2.3 Establishment of Methodology of Tiered Short-Term Exposure WQSs

The methodology of tiered short-term exposure WQSs was developed with the principle of SSD and ecological risk assessment. The SSD curve was fitted by the desirable SSD method that screened out through the above procedure. The tiered ecological risks were defined according to different affected fractions of species, and the corresponding pollutant concentrations were calculated by the fitting function. Then, the tiered short-term exposure WQSs were developed according to the tiered pollutant concentration and a correction factor.

2.4 Data Analysis and Development of Short-Term WQSs for Cd, Cu, Pb and Zn

The data were analyzed using the PASW statistics 18. The normality of the data was checked by Kolmogorov-Smirnov test. Statistical significances were considered to be significant at $p \leq 0.05$. The species acute toxicity data was used to generate the SSD curve. If a species has more than one toxicity datum, the species mean acute value (SMAV) was used instead, and it equal to the geometric average of all the qualified toxicity data of the species. According to the methodology that established above, the short-term exposure WQSs for the four heavy metals were developed. Finally, a case analysis of sudden cadmium pollution in Longjiang River, Guangxi Province in 2012 was performed with the derived short-term WQSs of cadmium.

3. Results

3.1 Freshwater Species Sensitivity of Cd, Cu, Pb and Zn

Published acute toxicity data of Cd, Cu, Pb and Zn to freshwater organisms were collected and screened, and the results were shown in the supplementary materials. Qualified toxicity data of 45 species for Cd^{2+}, 54 species for Cu^{2+}, 26 species for Pb^{2+} and 26 species for Zn^{2+} were obtained. The normality of these ecotoxicity data were analyzed by Kolmogorov-Smirnov test and the results showed that they are all acceptable.

The statistic characteristics of the qualified data were analyzed and the results were shown in Table 1. We can see that the data of Cu^{2+} is sufficient and the data of Pb^{2+} and Zn^{2+} is relatively insufficient. Fortunately, they all meet the minimum toxicity data requirement of SSD generation (ten data for fitting of one SSD curve (Wheeler, Grist, Leung, Morritt, & Crane, 2002). In term of the average value, Cu^{2+} has higher toxicity, while Pb^{2+} has lower toxicity to freshwater organisms.

Table 1. Statistic characteristics of toxicity data of Cd, Cu, Pb and Zn

Heavy metals	Sample number	Minimum/(μg/L)	Maximum/(μg/L) *	Average/(μg/L)	SD
Cd^{2+}	45	0.15	4.76	2.85	1.07
Cu^{2+}	54	-0.80	4.46	1.82	0.89
Pb^{2+}	26	1.80	5.84	3.78	1.23
Zn^{2+}	26	1.93	4.85	3.40	0.91

Note: The minimum value have been transformed by common logarithm.

As for the sensitivity of freshwater organism to the four heavy metals, the most sensitive and insensitive species to Cd^{2+} are *Salmo trutta* (LC_{50} = 1.40 μg/L) and *Branchiura sowerbyi* (LC_{50} = 58 020 μg/L), respectively. Except 1 fish and 1 rotifer, in the 10 most sensitive organisms to Cd^{2+}, the other 8 are all crustaceans. The most sensitive and insensitive species to Cu^{2+} are *Tubifextubifex* (LC_{50} = 0.16 μg/L) and *Sinopotamon henanense* (LC_{50} = 28 610 μg/L), respectively. Except the tubificid worm *Tubifex tubifex*, in the 10 most sensitive organisms to Cu^{2+}, the other 9 are all crustaceans. The most sensitive and insensitive species to Pb^{2+} are *Ceriodaphnia dubia* (LC_{50} = 63.8 μg/L) and *Sinopotamon henanense* (LC_{50} = 692 090 μg/L). The 10 most sensitive organisms to Pb^{2+} contain 5 crustaceans, 4 fish and 1 shrimp, indicating the diversity of species sensitivity to this heavy metal. The most sensitive and insensitive species to Zn^{2+} are *Ceriodaphnia reticulate* (LC_{50} = 85.4 μg/L) and *Rana catesbeiana* (LC_{50} = 70 000 μg/L), respectively. Except 1 fish and 1 rotifer, in the 10 most sensitive organisms to Zn^{2+}, the other 8 are all crustaceans. So, the SSD of the four heavy metals suggested that crustaceans may be the most sensitive species to heavy metals.

3.2 The Suitability of the Four SSD Methods

In order to screen the desired constuction method of SSD curve, four SSD fitting methods were adopted to analyze the acute toxicity data of the four heavy metals to acquire the HC_5 values. The results were shown in Table 2, and it suggested that different SSD method produced different HC_5 values. Generally, the values derived with "SSD-RIVM" and "SSD- AU & NZ" methods were relatively higher, while the "SSD-EU" method was relatively stringent.

Table 2. Comparison of the derived HC_5 values of the four SSD fitting methods

Fitting Methods	Fitting Functions	HC_5/(μg/L)			
		Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
SSD-USA	Log-triangular	4.32	3.32	88.54	90.14
SSD-EU	Log-logistic	0.72	0.26	10.28	23.19
SSD-RIVM	Log-normal	12.09	2.19	54.26	75.71
SSD-AU & NZ	BurrIII	9.42	3.22	110.26	115.31

Note. The derivation of the fitting methods: SSD-USEPA (USEPA, 1985), SSD-EU (Aldenberg & Solb, 1993), SSD-RIVM (Aldenberg &Jaworska, 2000), SSD-AU & NZ (Hose & Van den Brink, 2004).

The "SSD-AU & NZ" method was chosen as a desirable fitting method for its moderate derived values to develop the methodology of the short-term WQSs.

3.3 Establishment of the Methodology of Tiered Short-term WQSs

The methodology of tiered short-term exposure WQSs were developed with the principle of SSD and ecological risk assessment. Different affected fraction of the aquatic organism corresponds to different ecological risk level caused by the pollutant. In the Netherlands, if the affected fraction of the aquatic species reaches 50%, the risk level caused by the pollutant is considered serious (Traas, 2001). On the other hand, if the affected fraction of the aquatic species less than 5%, the ecological risk posed by the pollutant can be ignored generally (USEPA, 1985). Taking the above principles as references, four grades of risk levels were designed in this study according to different affected fractions of the aquatic species, and the corresponding four grades of short-term WQSs were derived. As shown in Figure 1, they are "4^{th} grade (IV)" (serious risk, the affected fraction is greater than 50%), "3^{rd} grade (III)" (apparent risk, the affected fraction is greater than 30%), "2^{nd} grade (II)" (some risk, the affected fraction is greater than 15%) and "1^{st} grade (I)" (potential risk, the affected fraction is greater than 5%). The X value in Figure 1 indicates the hazardous concentration (Shcheglov, Moiseichenko, & Kovekovdova, 1990) of the pollutant, and the WQS equals the HC value divided by the correction factor that was generally assumed to be 1 to 5 (van Vlaardingen & Verbruggen, 2007). Because the uncertainty of the ecological risk rise with the increasing of concentration of pollutant, the correction factor value was set to be 5, 4, 3 and 2, corresponding to the four grades of WQSs, IV, III, II and I, respectively.

In addtion, the short-term duration time and frequency of the derived WQSs in this study were designated "3 hrs" and "not more than one time pre three years" according to the technical guidelines of the US (USEPA, 1985). They were proposed according to the results of related sciencititic research that concerned the toxic effects of pollutant to individual species and ecosystem.

3.4 Derivation of the Tiered Short-term WQS for Heavy Metals

The tiered short-term WQS for the four heavy metals were derived according to the established methodology. The calculated SSD parameters were shown in Table 3, and the results were shown in Figure 2 and Table 4.

Table 3. The SSD parameters calculated with "SSD-AU & NZ" method

Heavy Metals	Fitting Functions	Calculated SSD parameters		
Cd^{2+}	BurrIII	1122.381 (*b*)	0.745 (*c*)	0.834 (*k*)
Cu^{2+}	BurrIII	24.957 (*b*)	0.791 (*c*)	1.662 (*k*)
Pb^{2+}	ReWeibull	21.158 (α)	0.415 (β)	
Zn^{2+}	ReWeibull	38.224 (α)	0.536 (β)	

Table 4. The four-grade short-term exposure WQSs of the heavy metals

Grades	Risks	Affected Fraction	Short-term exposure WQSs/(μg/L)			
			Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
IV	Serious	50%	158	11.5	746	353
III	Apparent	30%	58.1	5.80	247	157
II	Some	15%	20.5	3.20	110	90.1
I	Potential	5%	4.71	1.61	55.1	57.7

3.5 Case Analysis with the Developed Short-term WQSs of Cadmium

A sudden cadmium environmental pollution was occurred in Longjiang River, Guangxi Province in China in 2012. The reported peak values of cadmium concentration exposed in the river in the accident was 400 μg/L, and after emergency disposal, it decreased to about 125 μg/L (Xinhua News Agency reported). In term of the short-term WQSs of cadmium developed in this study, the 400 μg/L of cadmium may pose serious ecological risks (risk grade: IV), and most of the regional aquatic species are threatened, while the 125 μg/L of cadmium may pose apparent ecological risks (risk grade: III) and the affected aquatic species is greater than 30% (Table 4 and Figure 2). The affected organisms contained shrimps, some sensitive fish, e.g. the bighead fish, and some aquatic invertebrates, such as hydras, daphnia and rotifers. Basically, after emergency disposal, there were no risks to some insensitive species, such as common carp, loach, amphibians, oysters and crabs with the time limitation of 3 hrs.

4. Discussion

WQSs play important role in water environment management. They can be divided into long term exposure WQS and short term exposure WQS (USEPA, 1985). Generally, the value of the former are lower, and they are determined according to the results of WQC study, risk assessment and cost-benefit analysis etc (USEPA, 1994), while the value of the latter are higher, and they are developed according to the results of WQC study and risk assessment (van Vlaardingen & Verbruggen, 2007; Sloof, 1992). Compared with WQC from USEPA (2009), WQS of grade I for the four heavy metals in our study is in the same order of magnitude. Grade I for Cd^{2+} is slightly higher than CMC in America, and grade I for Pb^{2+} is slightly lower. CMC of Zn^{2+}in America was between 90.1μg/L of Grade II and 157μg/L of Grade III in our study. However, grade IV for $Cu^{2+}$is still lower than that in America, indicating that Chinese native species were more sensitive to Cu^{2+}.

As for the minimum toxicity data requirement for deriving the WQC, the USEPA prescribed that at least three phyla and eight families should be used in the calculation (USEPA, 1985). The short term exposure WQS were divided into two sorts, A and B, in the WQS guidelines issued by the Canadian Council of Ministers of the Environment (CCME, 2007). The WQS of sort A should be developed by the SSD method with sufficient toxicity data that at least include data of 3 fish (including 1 Salmonidae fish and 1 non-Salmonidae fish), 3 aquatic or semi-aquatic invertebrate (including 1 pelagic crustacean) and if have, aquatic plants and amphibian. When the toxicity data is insufficient, the assessment factor (AF) method was recommended to derive the WQS of sort B. In the guidance for derivation of environmental risk limits issued by the Netherlands (van Vlaardingen & Verbruggen, 2007), according to different situations, three methods, the AF method, the SSD method and simulation of ecosystem were recommended to develop the short term WQS, respectively. In the guidance, at least three acute toxicity data of three different trophic level (for example, algae, daphnia and fish), are required to be used in the AF method, and at least eight acute toxicity data of aquatic organisms, including 6 aquatic animals, 1 algae and 1 higher plant, are required to be used in the SSD method. Two kinds of vertebrate, including 1 fish should be contained in the 6 aquatic animals. In the present study, sufficient toxicity data were collected for all the four heavy metals, and the data quantity is qualified for all the SSD methods.

There are several popular SSD methods for derivation of the WQSs, and all of them were accepted by the Organization for Economic Co-operation and Development (OECD, 1992; Posthuma, Suter, & Traas, 2002). These SSD methods were evaluated in the present study with calculation of the HC_5 value. Through comparison analysis, the “SSD-AU & NZ” method produced relatively moderate results for all the four heavy metals and was chosen to derive the WQS in this study. The derived short term exposure WQS was set to four grades (I, II, III and IV) in this study. The correct factors for the HC values were set to be 2, 3, 4 and 5 for the four grades of risks due to the increasing risks with the higher pollutant concentrations, and they still need to be validated in field study or management of sudden environmental pollution accident.

According to the methodology of the short-term WQSs, the duration time is 3 hrs. In an accident of sudden environmental pollution, when the exposure time beyond 3 hrs, the posed ecological risk could be increased. How to assess the increased risks in an emergency is worth study. Before a perfect theory being proposed, at least some aquatic organisms can be taken as biological indicators for risk assessment. For example, in the above case analysis of the accident of the Longjiang River cadmium pollution, according to the Table S1 (supplementary materials) and figure 2, we can know that when the sensitive freshwater shrimps were hard to survive, the pollutant can be considered to have posed some ecological risks, and the death of bighead fish and amphibians indicate apparent and serious risks, respectively.

Generally, the ecotoxicity of heavy metals can be affected by some water quality parameters, such as hardness, temperature, pH, etc. So a perfect WQS should be developed according to different regional water conditions. Moreover, the water quality conditions in different basins or regions in China are of high diversity. WQSs should be developed according to different ecoregions to facilitate risk assessment, ecoregion protection and environmental management in pollution accident. The derived WQSs in the present study may be improved in these aspects in the future.

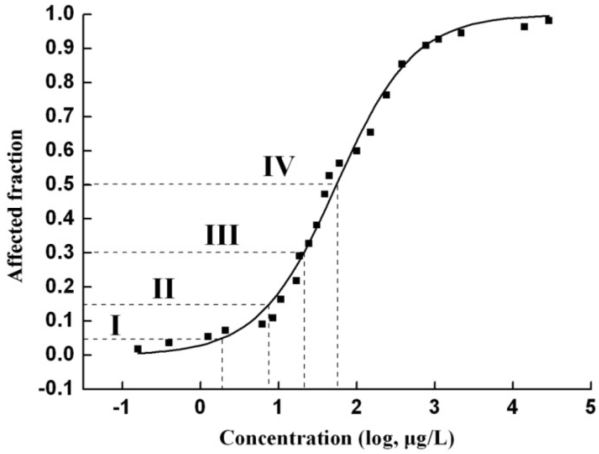

Figure 1. Sketch map of SSD curve fitting

Note. "I", "II", "III" and "IV" in the figure represents the four grade WQSs, and is corresponding to the four grade ecological risk levels: I (potential risk, the affected fraction is greater than 5%), II (some risk, the affected fraction is greater than 15%), III (apparent risk, the affected fraction is greater than 30%) and IV (serious risk, the affected fraction is greater than 50%).

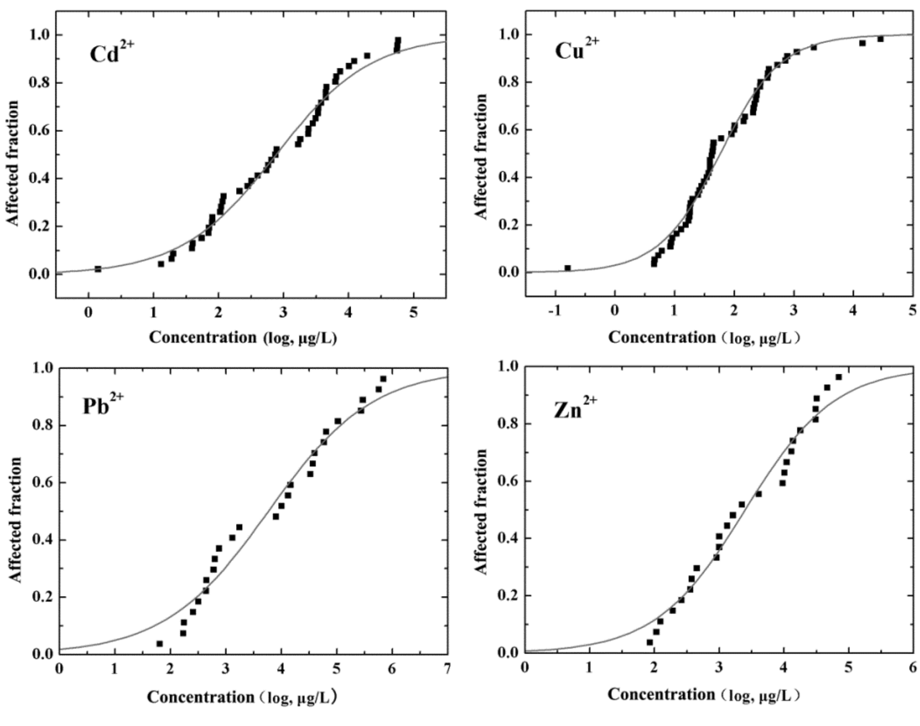

Figure 2 SSD fitting of four heavy metals

Note. The solid square in the figure indicate the acute ecotoxicity data of different heavy metals.

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