

Chapter 2

Development of Emergency Water Quality Standard for Typical Heavy Metals with Chinese Resident Ecotoxicity Data

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Abstract Environmental pollution emergency of heavy metals has posed serious ecological risks in China. However, local emergency water quality standards (WQSs) are not yet established. In the present study, local ecotoxicity data of six heavy metals, Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Hg^{2+} and Cr^{6+} , were collected and screened. The suitability of four species sensitivity distribution (SSD) methods assumed to be used to derive the WQSs was evaluated by data analysis. Then, the methodology of emergency WQSs was established with the principles of SSD and ecological risk assessment, and the tiered emergency WQSs values of the six heavy metals were derived with the established methodology. Finally, a case analysis was demonstrated with the developed cadmium emergency WQSs and risk grade definition. The results may provide technical references for response to environmental pollution emergency.

Keywords Emergency · Water quality criterion · Water quality standard · Ecological risk assessment · Heavy metals

2.1 Introduction

Water quality standards (WQSs) form the foundation of discharge standards of pollutants and protection of ambient water environment quality. They can be divided into long-term exposure WQSs and short-term (emergency) 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

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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 (ANZECC and ARMCANZ 2000) and the negligible concentration (NC), the maximum permissible concentration (MPC), and the serious risk concentration (SRC) issued by the Netherland (Traas 2001).

The emergency WQSs were studied earlier in the United States. 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 United States (USEPA 2009). In recent years, many countries strengthen the study on the emergency WQSs. For example, the Netherlands 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.

After decades of development, China has established relatively mature long-term exposure WQSs to protect the quality of surface water, groundwater, marine water, and so on. However, emergency 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. For example, recently, the serious sudden accident of pollution of cadmium taking place in the Longjiang River in Guangxi Province has caused tens of tons of adult fish and more than one million of fry to death (Xinhua News Agency reported). The emergency WQSs are needed urgently in China to assess the ecological risk posed by heavy metals in emergency pollution accidents. This study collected and screened the acute ecotoxicity data of six heavy metals and established the methodology of emergency WQSs with the principle of species sensitivity distribution (SSD) and ecological risk assessment. And, the tiered emergency WQSs for six typical heavy metals were derived. The results can provide valuable information to the environmental management of sudden pollution accident of heavy metals.

2.2 Materials and Methods

2.2.1 *Collection of Published Acute Ecotoxicity Data of Six Heavy Metals*

The published acute toxicity data of Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Hg^{2+} , and Cr^{6+} 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 national WQC for the protection of aquatic organisms and their uses in the United States (USEPA 1985). Unqualified data with unsuitable exposure time, unusual diluted 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-LC₅₀ or EC₅₀ for daphnia or larvae of midge, and 96 h-LC₅₀ or EC₅₀ for fish, mollusks, shrimp, and other organisms were chosen.

2.2.2 *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 emergency WQs was evaluated. The hazardous concentrations for 5 % of the species (HC₅) were calculated according to four SSD methods that are based on log-triangle (USEPA 1985), log-normal (Van Vlaardingen et al. 2004), log-logistic (Aldenberg and Solb 1993), and BurrIII function (Hose and Van den Brink 2004), respectively. The model that gained a suitable HC₅ value was chosen to derive the pollutant concentration corresponding to different affected fractions of species.

2.2.3 *Establishment of Methodology of Tiered Emergency WQs*

The methodology of tiered emergency WQs was developed with the principle of SSD and ecological risk assessment. The SSD curve was fitted by the desirable SSD method that screened out in 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 emergency WQs were developed on the basis of the tiered pollutant concentration and a correction factor.

2.2.4 Data Analysis and Development of Emergency WQSs of Six Heavy Metals

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 were 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 is equal to the geometric average of all the qualified toxicity data of the species. According to the methodology established above, the emergency WQSs for the six heavy metals were developed. Finally, a case analysis of sudden cadmium pollution in Longjiang River, Guangxi Province, in 2012 was demonstrated with the derived emergency WQSs of cadmium.

2.3 Results

2.3.1 Freshwater Species Sensitivity of the Six Heavy Metals

Published acute toxicity data of six heavy metals to freshwater organisms were collected and screened, and the results were shown in the supporting materials. Qualified toxicity data of 45 species for Cd^{2+} , 54 species for Cu^{2+} , 26 species for Pb^{2+} , 26 species for Zn^{2+} , 47 species for Hg^{2+} , and 30 species for Cr^{6+} were obtained. The normality of these ecotoxicity data was 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 2.1. We can see that the data of Cu^{2+} are sufficient and the data of Pb^{2+} and Zn^{2+} are relatively insufficient. Fortunately, they all meet the minimum toxicity data requirement of SSD generation [ten data for fitting of one SSD curve (Wheeler et al. 2002)]. In terms of the average value, Cu^{2+} and Hg^{2+} have higher toxicity, while Pb^{2+} and Cr^{6+} have lower toxicity to freshwater

Table 2.1 Statistic characteristics of toxicity data of the six heavy metals

Heavy metals	Sample number	Minimum ($\mu\text{g/L}$) ^a	Maximum ($\mu\text{g/L}$) ^a	Average ($\mu\text{g/L}$)	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
Hg^{2+}	47	−0.52	4.23	2.00	1.01
Cr^{6+}	30	0.48	5.54	3.61	1.49

^aThe data have been transformed by common logarithm

organisms. The standard deviation (SD) of the data set of Cr^{6+} (1.49) is the highest, and that of Cu^{2+} (0.89) is the lowest.

As for the sensitivity of freshwater organism to the six heavy metals, the most sensitive and insensitive species to Cd^{2+} are *Salmo trutta* ($\text{LC}_{50} = 1.40 \mu\text{g/L}$) and *Branchiurusowerbyi* ($\text{LC}_{50} = 58,020 \mu\text{g/L}$), 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 *Tubifex tubifex* ($\text{LC}_{50} = 0.16 \mu\text{g/L}$) and *Sinopotamon henanense* ($\text{LC}_{50} = 28,610 \mu\text{g/L}$), 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* ($\text{LC}_{50} = 63.8 \mu\text{g/L}$) and *Sinopotamon henanense* ($\text{LC}_{50} = 692,090 \mu\text{g/L}$). 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 reticulata* ($\text{LC}_{50} = 85.4 \mu\text{g/L}$) and *Ranacates beiana* ($\text{LC}_{50} = 70,000 \mu\text{g/L}$), respectively. Except 1 fish and 1 rotifer, in the 10 most sensitive organisms to Zn^{2+} , the other 8 are all crustaceans. The most sensitive and insensitive species to Hg^{2+} are *Ictalurus punctatus* ($\text{LC}_{50} = 0.30 \mu\text{g/L}$) and *Rana tigrina* ($\text{LC}_{50} = 17,165 \mu\text{g/L}$), respectively. Except 2 fish, in the 10 most sensitive organisms to Hg^{2+} , the other 8 are all crustaceans. The most sensitive and insensitive species to Cr^{6+} are *Diaphanosoma brachyurum* ($\text{LC}_{50} = 3.00 \mu\text{g/L}$) and *Cyprinus carpio* ($\text{LC}_{50} = 346,700 \mu\text{g/L}$). The 10 most sensitive organisms to Cr^{6+} are all crustaceans. So, the SSD of the six heavy metals suggested that crustaceans are the most sensitive species to heavy metals.

2.3.2 The Suitability of the Four SSD Methods Assumed to Be Used to Develop the Methodology

In order to screen the desired construction method of SSD curve, four SSD fitting methods were adopted to analyze the acute toxicity data of the six heavy metals to acquire the HC_5 values. The results were shown in Table 2.2, 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.

2.3.3 Establishment of the Methodology of Tiered Emergency WQSs

The methodology of tiered emergency WQSs was developed with the principle of SSD and ecological risk assessment. Different affected fraction of the aquatic

Table 2.2 Comparison of the derived HC₅ values of the four SSD fitting methods

Fitting methods	Fitting functions	HC ₅ (μg/L)					
		Cd ²⁺	Cu ²⁺	Pb ²⁺	Zn ²⁺	Hg ²⁺	Cr ⁶⁺
SSD-USA ^[2]	Log-triangular	4.32	3.32	88.54	90.14	0.86	7.28
SSD-EU ^[11]	Log-logistic	0.72	0.26	10.28	23.19	0.54	0.74
SSD-RIVM ^[16]	Log-normal	12.09	2.19	54.26	75.71	2.16	13.40
SSD-AU & NZ ^[12]	BurrIII	9.42	3.22	110.26	115.31	1.16	1.34

The “SSD-AU & NZ” method was chosen as a desirable fitting method for its moderate derived values to develop the methodology of the emergency WQSs

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 is 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 emergency WQSs were derived. As shown in Fig. 2.1, they are “4th grade (IV)” (serious risk, the affected fraction is greater than 50 %), “3rd grade (III)” (apparent risk, the affected fraction is greater than 30 %), “2nd grade (II)” (some risk, the affected fraction is greater than 15 %), and “1st grade (I)” (potential risk, the affected fraction is greater than 5 %). The X value in Fig. 2.1 indicates the hazardous concentration (Shcheglov et al. 1990) of the pollutant, and WQS equals the HC value divided by the correction factor that was

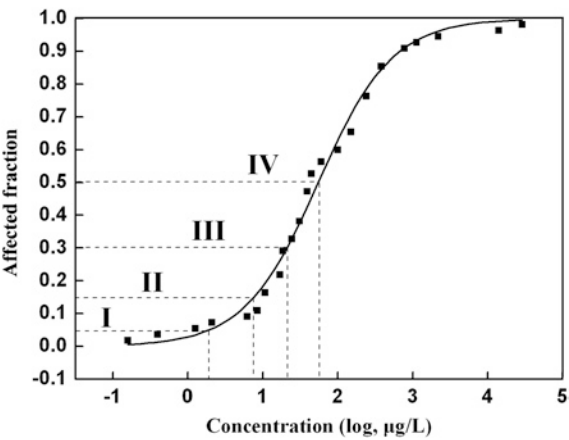


Fig. 2.1 Sketch map of SSD curve fitting. “I”, “II”, “III,” and “IV” in the figure represent the four-grade WQSs and is corresponding to the four grades of ecological risk levels: I (potential risk, the affected fraction is greater than 5 %), II (some risk, the affected fraction is greater than 15 %), III (apparent risk, the affected fraction is greater than 30 %), and IV (serious risk, the affected fraction is greater than 50 %)

generally assumed to be 1–5 (van Vlaardingen and Verbruggen 2007). Because the uncertainty of the ecological risk rises with the increase of concentration of pollutant, the correction factor value was set to be 5, 4, 3, and 2, corresponding to the four grades of WQSSs, IV, III, II, and I, respectively.

In addition, the emergency duration time and frequency of the derived WQSSs in this study were designated “3 h” and “not more than one time pre-three years” according to the technical guidelines of WQC in the USA (USEPA 1985; Jin et al. 2009). They were proposed according to the results of related scientific research that concerned the toxic effects of pollutant to individual species and ecosystem.

2.3.4 Derivation of the Tiered Emergency WQS for Heavy Metals

The tiered emergency WQS for the six heavy metals was derived according to the established methodology. The calculated SSD parameters were shown in Table 2.3, and the results were shown in Fig. 2.2 and Table 2.4.

2.3.5 Case Analysis with the Developed Emergency WQSSs of Cadmium

A sudden cadmium environmental pollution was occurred in Longjiang River, Guangxi Province, in China in 2012. The reported peak value 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 terms of the emergency WQSSs 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 2.4; Fig. 2.2). The affected organisms contained shrimps, some sensitive fish, e.g., the bighead fish, and some aquatic invertebrates, such as hydras,

Table 2.3 The SSD parameters calculated with “SSD-AU & NZ” method

Heavy metals	Fitting functions	Calculated SSD parameters		
Cd ²⁺	BurrIII	1122.381 (<i>b</i>)	0.745 (<i>c</i>)	0.834 (<i>k</i>)
Cu ²⁺	BurrIII	24.957 (<i>b</i>)	0.791 (<i>c</i>)	1.662 (<i>k</i>)
Pb ²⁺	ReWeibull	21.158 (α)	0.415 (β)	
Zn ²⁺	ReWeibull	38.224 (α)	0.536 (β)	
Hg ²⁺	BurrIII	599.347 (<i>b</i>)	1.496 (<i>c</i>)	0.320 (<i>k</i>)
Cr ⁶⁺	BurrIII	217341.131 (<i>b</i>)	3.834 (<i>c</i>)	0.065 (<i>k</i>)

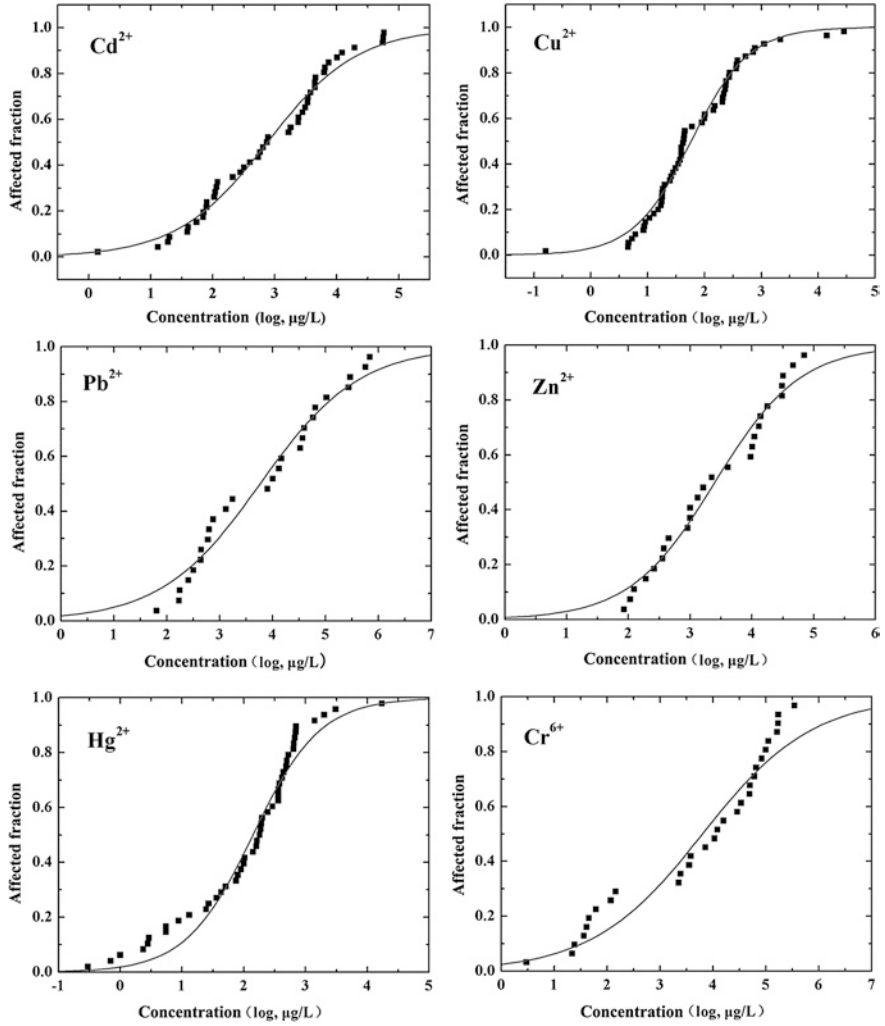


Fig. 2.2 SSD fitting of six heavy metals. The *solid square* in the figure indicates the acute ecotoxicity data of different heavy metals

Table 2.4 The four-grade emergency WQs of the heavy metals

Grades	Risks	Affected fraction (%)	Emergency WQs (μg/L)					
			Cd ²⁺	Cu ²⁺	Pb ²⁺	Zn ²⁺	Hg ²⁺	Cr ⁶⁺
IV	Serious	50	158	11.5	746	353	30.6	2,702
III	Apparent	30	58.1	5.80	247	157	12.3	436
II	Some	15	20.5	3.20	110	90.1	3.80	36.2
I	Potential	5	4.71	1.61	55.1	57.7	0.580	0.67

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 h.

2.4 Discussions

WQSs play important role in water environment management. They can be divided into long-term exposure WQS and emergency WQS (USEPA 1985). Generally, the value of the former is lower, and they are determined according to the results of WQC study, risk assessment, and cost–benefit analysis (USEPA 1994), while the value of the latter is higher, and they are developed according to the results of WQC study and risk assessment (Van Vlaardingen and Verbruggen 2007; Sloof 1992).

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, and the details of the aquatic animals are contained in the aquatic life criteria guidelines (USEPA 1985). The emergency WQS were divided into two sorts, A and B, in the WQS guidelines issued by the CCME (2007). The WQS of sort A should be developed by the SSD method with sufficient toxicity data at least from three fish (including One Salmonidae fish and One non-Salmonidae fish), three aquatic or semi-aquatic invertebrate (including one pelagic crustacean), and if possible, aquatic plants and amphibian. When the toxicity data are 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 and Verbruggen 2007), according to different situations, three methods, the AF method, the SSD method, and simulation of ecosystem, were recommended to develop the emergency WQS, respectively. In the guidance, at least three acute toxicity data of three kinds of different trophic level, such as 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 six 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 Cooperation and Development (OECD 1992; Posthuma et al. 2002). These SSD methods were evaluated in the present study with calculation of the HC₅ value. Through comparison analysis, the “SSD-AU & NZ” method produced relatively moderate results for all the six heavy metals and was chosen to derive the WQS in this study. The derived emergency 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 emergency environmental accident.

According to the methodology of the emergency WQSs, the duration time is 3 h. In an accident of emergency environmental pollution, when the exposure time is beyond 3 h, 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 Fig. 2.2, we can know that when the sensitive freshwater shrimp is hard to survive, the pollutant can be considered to have posed some ecological risks, and the death of bighead fish and amphibians indicates apparent and serious risks, respectively.

Generally, the ecotoxicity of heavy metals can be affected by some water quality parameters, such as hardness, temperature, and pH. 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 emergency accident. The derived WQSs in the present study may be improved in these aspects in the future.

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