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# Setting Water Quality Criteria in China: Approaches for Developing Species Sensitivity Distributions for Metals and Metalloids

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## 1 Introduction

Water quality criteria (WQCs) refer to the maximum acceptable concentrations of specific chemicals or magnitudes of parameters in water that protect aquatic life and human health under certain conditions (USEPA 1976). When deriving WQC for use in regional ecosystems, sociopolitical and economic factors need to be considered (Meng and Wu 2010). The WQC concept is often used for making policy, managing the environment, assessing water quality, controlling pollution, restoring ecosystems, and managing environmental crises (Wu et al. 2010). Some countries and organizations have created WQC guidelines that describe what is suitable for the specific conditions prevalent in that country or region. Since the 1960s, the United States has undertaken a series of long-term studies to develop national WQC for specific water pollutants that threaten aquatic organisms and human health (USEPA 1968, 1976, 1986, 1999, 2002, 2004, 2009). In the past few decades, Australia, Canada, the European Union, the Netherlands, and the World Health Organization have, respectively, developed their own WQCs to protect national or regional water environments (CCME 1999; ANZECC and ARMCANZ 2000; ECB 2003; WHO 2006; RIVM 2007).

As a country with rich aquatic species and vast freshwater regions, China also plays an important role in protecting its share of the world aquatic ecosystems. However, the water environment of China is suffering from contamination with metals and metalloids that has and is being released from human activities; much of this contamination is a consequence of China's rapid economic development and the expansion of its human population. Like other countries, China manages water quality by establishing or adopting water quality standards. However, the WQC standards for other countries may not be wholly appropriate for conditions in China. WQCs that are specific to certain geographic regions, other than China, and the species composition therein may not be appropriate for managing the environment in China. Thus, it is urgent to establish guidelines or WQCs that are based on the characteristics, composition, and distribution of aquatic species endemic to China.

Information on the toxicity of chemicals to aquatic organisms that is applied in ecological risk assessments usually comes from tests with single species. However, the entity to be protected is not limited to individuals but rather extends to populations, communities, and ecosystems. Species sensitivity distributions (SSDs) are useful for extrapolating between the macro-scale (such as communities) and the microscale (such as individuals) in an integrative risk assessment across temporal and spatial scales (Newman et al. 2000). As an efficient tool for ecological risk

assessment, SSDs have received considerable attention since the 1980s (Stephan et al. 1985; Aldenberg and Slob 1993). SSDs are used to investigate relationships among sensitivities of species to environmental stressors, such as metals and organic chemicals. The primary purpose of establishing SSDs is to determine the tolerated concentration of a substance for protecting individuals of a defined proportion of a species found in an assemblage (usually 95%), and this tolerated concentration may be hazardous to 5% of total species (HC5) (van Straalen and Denneman 1989). For this purpose, SSDs are visualized as a plot of a cumulative distribution function against the logarithm of the concentrations of toxicity data (Solomon et al. 2000). Also, SSDs offer greater statistical confidence in calculating a predicted no effect concentration (PNEC) for use in risk assessments than does the commonly used quotient approaches (Grist et al. 2002; Wheeler et al. 2002; Wang et al. 2008). The latter approaches are usually calculated by applying a safety factor to the statistical summary of a single toxicity test such as no observed effect concentration (NOEC) or a 50%-effect concentration ( $EC_{50}$ ) (van Dam et al. 2012).

When constructing SSDs, there are no standard approaches to achieve fits to all toxicity data. However, several approaches have been applied to develop SSDs and to estimate HC5 values, which include Burr Type III (Shao 2000), Gompertz (Newman et al. 2000), log-logistic, lognormal (Pennington 2003), and Weibull (van Straalen 2002). A recent study reported and compared the array of statistical distributions used to analyze air contaminant data (Marchant et al. 2013). The common characteristic of these approaches is the assumption that species sensitivities follow certain specific statistical distributions. However, this assumption is often violated due to statistical limitations resulting from deviations between theoretical and empirical data (Forbes and Forbes 1993; Calow 1996; Power and McCarty 1997; Grist et al. 2002). In practice, a majority of the data selected usually do not meet all assumptions. For instance, the most commonly used lognormal distribution failed to fit the toxicity data on a number of occasions (Newman et al. 2000). To resolve this limitation in deriving HC5 values for contaminants, without making any assumptions about the underlying distributions, use of a more robust nonparametric method, known as bootstrap, has been suggested. Bootstrap resampling methods were first used to estimate HC5 values of pesticide by constructing SSDs (Jagoe and Newman 1997; Newman et al. 2000). The bootstrap regression was further developed by combining a nonparametric bootstrap with a parametric log-logistic model to solve the difficulty of the limited toxicity data available (Grist et al. 2002). Based on the standard bootstrap, we applied artificial interpolations to avoid repetitive values in each resample and to expand the data beyond the limited original datasets (Wang et al. 2008).

Metals and metalloids (Power and McCarty 1997; Duffus 2002; Batley 2012; Chapman 2012) are widely distributed in the environment and can adversely affect the diversity and the evolution of aquatic organisms (Shaw and Grushkin 1957; Campbell and Stokes 1985; Mance 1987). For instance, cadmium is a typical metal pollutant that has been associated with many epidemiological diseases such as the *itai-itai* disease in Japan (Nogawa and Kido 1993). Although zinc is an essential element for many metabolic functions of most organisms, it is toxic to aquatic life when concentrations exceed the threshold for effects (Van Sprang et al. 2009;

Tsushima et al. 2010). The first WQC guideline for metals was developed by the USEPA in 1976; WQCs were developed for 12 metals and metalloids. Thus far, WQCs of 167 typical water pollutants have been established and these pollutants have been divided into priority and non-priority toxic classes (USEPA 1976, 1986, 1999, 2002, 2004, 2009). However, only 16 WQC values have been promulgated for protecting aquatic organisms, which include 11 for priority toxic metals and metalloids and 4 for non-priority metals (USEPA 1985; Meng and Wu 2010). SSDs have been applied in ecological risk assessments for freshwater environments, predominantly for single metals or organic pesticides. However, the reported works on SSDs have primarily focused on single metals or organic molecules (Solomon et al. 1996; Giesy et al. 1999; Campbell et al. 2000; TenBrook et al. 2010; Vardy et al. 2011). These works have not included many systematic and comparative studies on SSDs or WQC values established for multiple metals and metalloids in aquatic environments.

One goal in this study is to compare different approaches for deriving WQCs through SSDs that are based on toxicity data of representative aquatic species in China. First, we employed parametric and nonparametric approaches to develop SSDs through fitting chronic toxicity values. We evaluated sensitivities of species exposed to various chemicals before selecting indicator species for chemical bio-monitoring in the water environments. We further compared the approaches by using several statistical indicators to evaluate the applicability of different approaches. Criteria for model selection were further addressed by evaluating other data parameters, including species amounts and composition, species sensitivity, and geographic structure of aquatic habitats. Differences between the WQC values we derived to meet salient needs in China were then compared to those promulgated by selected other countries. Another study goal is to determine the risk of eight metals and metalloids to Chinese aquatic species by using Tai Lake (Ch: *Taihu*) as a study area. We performed the risk assessment of the metals and metalloids to aquatic species in Tai Lake by utilizing the measured exposure concentration (MEC) and WQC values derived from SSDs created by using different approaches.

## 2 Data Selection and Analysis

### 2.1 Data Collection

#### 2.1.1 Toxicity Data

Chronic toxicity data for aquatic species were used for constructing SSDs. The toxicity data from the literature that was used for the species and chemicals are shown in Table 1. All data were collected from the ECOTOX database of the USEPA (<http://www.epa.gov/ecotox>) and the database of the China National Knowledge Infrastructure (CNKI, <http://www.cnki.net/>). Accuracy, reliability, and relevance of

**Table 1** Statistical summary of toxic effects of metals and metalloids on freshwater species

| Metals and metalloids | Number of species | Exposure time (days) | Log transformation of toxicity and standard deviation (SD) ( $\mu\text{g/L}$ ) |      |                                    |
|-----------------------|-------------------|----------------------|--|------|------------------------------------|
|                       |                   |                      | Geometric mean   | SD   | <i>p</i> -value for normality test |
| As                    | 17                | 8~24                 | 2.46   | 0.64 | 0.652                              |
| Cd                    | 22                | 4~36                 | 0.31   | 0.15 | 0.757                              |
| Cr                    | 27                | 4~36                 | 1.64   | 0.65 | 0.366                              |
| Cu                    | 14                | 6~24                 | 2.65   | 0.67 | 0.841                              |
| Hg                    | 26                | 4~24                 | 0.59   | 0.24 | 0.724                              |
| Ni                    | 29                | 4~18                 | 2.65   | 0.42 | 0.452                              |
| Pb                    | 28                | 4~24                 | 1.64   | 0.64 | 0.566                              |
| Zn                    | 49                | 4~36                 | 2.86   | 0.37 | 0.578                              |

the literature data were evaluated by using standard methods (Klimisch et al. 1997; ECB 2003). The selected metalloid was arsenic (As), and the metals included cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) (Table 1). The species selected for developing the WQC were designed to represent examples that were widely distributed in aquatic ecosystems of China. The list included both native species and those originally imported from other countries but have now become widespread in China. The toxicity endpoints selected for deriving WQC were growth and reproductive effects. Toxicological tests of the literature data were performed according to standard operational procedures. Duration of chronic toxicity data ranged from 4 to 36 days. Toxicity threshold values were calculated and reported either as the no observed concentration (NOEC) or the lowest observed effect concentration (LOEC). Geometric means were calculated for values having multiple reports with the same exposure time (Stephan et al. 1985). When several eligible chronic toxicity data for the same species are available, the NOEC value having the longest duration of exposure was selected for use. When the NOEC value was not available, the geometric mean of the LOEC was selected. When only the LOEC value was available, we regarded half of its value as the NOEC (Balk et al. 1995).

### 2.1.2 Measured Exposure Concentrations

Surface waters were collected from 40 sites in Tai Lake during September 2010 (Fig. 1). The sampling sites were recorded by using a global positioning system. The concentrations in water of seven metals and one metalloid (viz., As, Cr, Cd, Cu, Hg, Ni, Pb, and Zn) were measured by inductively coupled plasma-optical emission spectrometry (ICP-MS, Agilent, 7500 CX, USA) and atomic fluorescence spectrophotometer (AFS, AF-610A, China). MECs were calculated and used to assess risks of the metals to aquatic species living in Tai Lake.

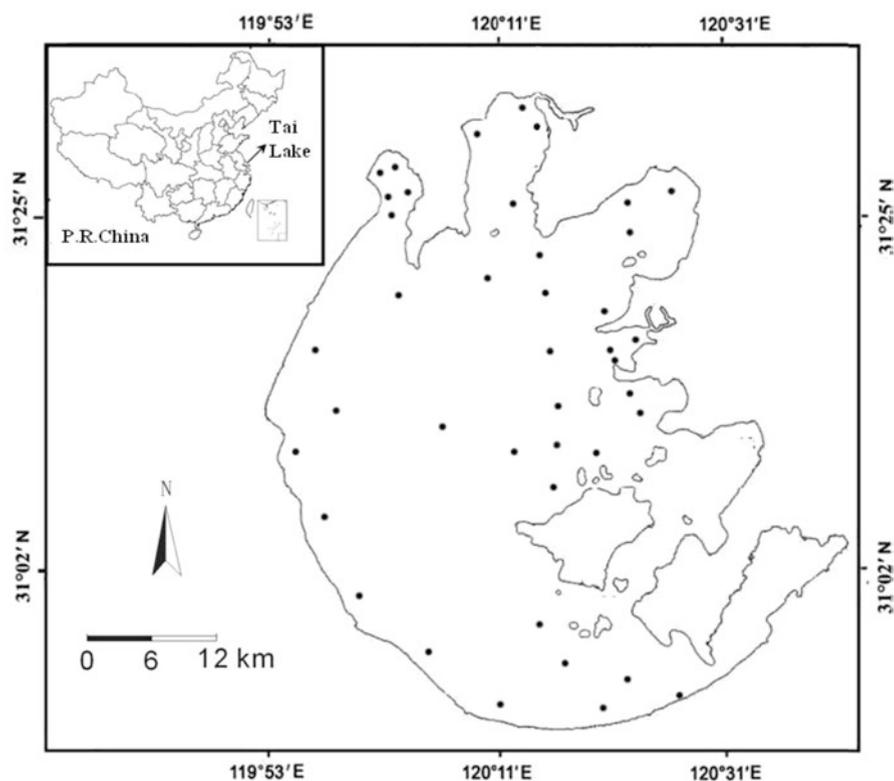


Fig. 1 Location of 40 sampling sites in the Tai Lake (*dark points* indicate sampling sites)

## 2.2 Methods Used to Construct SSDs

### 2.2.1 Parametric Approaches

After log transformation of effect concentrations (Stephan et al. 1985; Aldenberg and Jaworska 2000; van Straalen 2002), the Shapiro–Wilk test was performed on the SPSS Version 17 software to check the normality of toxicity and their applicability to four parametric approaches, including Gompertz (Newman et al. 2000), log-logistic (Aldenberg and Slob 1993; Pennington 2003), lognormal (Wagner and Løkke 1991; Wheeler et al. 2002), and sigmoid (Wu et al. 2011). These approaches were generally applicable for fitting species sensitivity data for species toxicity datasets of metals and metalloids. The toxicity data were fitted to the four statistical distributions, and the HC5 values were generated from the curves where the cumulative probability was equal to 0.05 (Posthuma et al. 2002).

### 2.2.2 Bootstrap

The bootstrap method is a nonparametric technique for simulating any statistical distribution through resampling of observed datasets, without assuming an underlying distribution or specific curve-fitting parameters in the model (Efron and Tibshirani 1993; Varian 2005). For example, suppose that an empirical toxicity sample  $t = [x_1, \dots, x_n]$  was first randomly or independently collected from a given population. A sample of size  $n$ ,  $t_1^* = [x_{11}^*, \dots, x_{1n}^*]$ , was further drawn from the members of  $t$  with replacement. Each observation  $x_i$  would be sampled with an equal replacement probability of  $1/n$ . The sampling process was iterated  $B$  times, and the  $B$ th bootstrap sample was marked as  $t_b^* = [x_{b1}^*, \dots, x_{bn}^*]$ . The number of iterations taken in this study was set to 5,000 according to the previous report (Wang et al. 2008). The members of each bootstrap sample were sorted in ascending order. The cumulative probabilities of sorted toxicity data were calculated to derive SSDs.

The bootstrap is limited to the original observations, although it does not require any distribution for the data. It is not suitable for examining the statistical distribution of the largest or the smallest observations, since the bootstrap method never generates an observation either larger or smaller than the maximum or the minimum observation (Efron and Tibshirani 1993). The bootstrap works with discrete data to derive an HC5 value for a given dataset, although the dataset must contain at least  $100/5 = 20$  members (Grist et al. 2002). Alternatively, in practice, it is difficult to collect adequate sample sizes for most cases, which restricts application of bootstrap methods. In this study, to avoid picking repetitive numbers in each resample caused by the process of the basic bootstrap, a modified bootstrap approach was developed by inserting interval values between consecutive ascending toxicity data. The modified bootstrap was applied to generate the HC5 values and was simply called *bootstrap* in this study. The detailed processing procedure was performed according to previously described methods (Wang et al. 2008).

### 2.2.3 Bootstrap Regression

The bootstrap regression was developed by combining the modified bootstrap with a log-logistic regression to improve fitting of datasets. Here we chose the log-logistic regression to combine with the bootstrap, since the conventional SSD approach yielded a good fit to the data having a log-logistic curve fitted through nonlinear regression (Grist et al. 2002) (Table 2). Bootstrapping was computed by using the modified procedure described above.

The computational processes for the parametric and nonparametric approaches were performed by the use of R programming language (Version 2.14.0, R Development Core Team 2011). Three indicators, root mean square errors (RMSE), error sum of squares (SSE), and coefficients of determination ( $r^2$ ), were derived from the four parametric approaches, while two indicators, RMSE and SSE, were obtained from the nonparametric approaches. These indicators were used to compare outputs and check the adequacy of the candidate approaches. The model with

**Table 2** Comparison of the 5% hazardous concentration threshold (HC5) value to protect 95% of species, calculated by different approaches

|   | As     | Cd    | Cr    | Cu    | Hg    | Ni    | Pb    | Zn     |
|---|--------|-------|-------|-------|-------|-------|-------|--------|
| Sample size                                 | 17     | 22    | 27    | 14    | 26    | 29    | 28    | 49     |
| Gompertz $F(x) = ae^{-e^{-(x-x_0)/(-b)}}$   |        |       |       |       |       |       |       |        |
| <i>a</i>                                    | 1.09   | 1.15  | 1.16  | 1.67  | 0.94  | 1.05  | 0.99  | 1.02   |
| $x_0$                                       | 3.08   | 0.39  | 1.92  | 2.70  | 0.44  | 2.61  | 1.17  | 3.06   |
| <i>b</i>                                    | 1.08   | 0.99  | 0.95  | 1.54  | 0.59  | 0.92  | 0.73  | 0.91   |
| HC5   | 72.76  | 0.18  | 6.70  | 5.86  | 0.58  | 38.65 | 2.36  | 114.21 |
| $r^2$                                       | 0.97   | 0.98  | 0.99  | 0.94  | 0.99  | 0.99  | 0.99  | 0.99   |
| RMSE  | 0.05   | 0.04  | 0.04  | 0.08  | 0.03  | 0.02  | 0.03  | 0.03   |
| SSE   | 0.04   | 0.09  | 0.03  | 0.11  | 0.03  | 0.01  | 0.02  | 0.03   |
| Log-logistic $F(x) = 1/[1 + e^{(a-x)/b}]$   |        |       |       |       |       |       |       |        |
| <i>a</i>                                    | 3.54   | 5.46  | 2.15  | 2.54  | 1.38  | 3.68  | 1.79  | 3.87   |
| <i>b</i>                                    | 0.62   | 0.63  | 0.51  | 0.60  | 0.56  | 0.72  | 0.49  | 0.63   |
| HC5   | 50.83  | 0.23  | 4.42  | 5.89  | 0.53  | 36.03 | 2.23  | 111.9  |
| $r^2$                                       | 0.95   | 0.99  | 0.99  | 0.95  | 0.97  | 0.99  | 0.99  | 0.98   |
| RMSE  | 0.07   | 0.03  | 0.03  | 0.07  | 0.05  | 0.02  | 0.04  | 0.04   |
| SSE   | 0.06   | 0.06  | 0.02  | 0.09  | 0.07  | 0.01  | 0.03  | 0.07   |
| Lognormal (probit scale) $F(x) = ax + b$    |        |       |       |       |       |       |       |        |
| <i>a</i>                                    | 0.41   | 1.73  | 0.38  | 0.35  | 0.58  | 0.22  | 0.22  | 0.39   |
| <i>b</i>                                    | -2.42  | -0.27 | -1.98 | -1.94 | -1.48 | -1.96 | -1.75 | -2.43  |
| HC5   | 80.75  | 0.16  | 7.53  | 6.85  | 0.52  | 28.76 | 2.94  | 103.75 |
| $r^2$                                       | 0.95   | 0.94  | 0.87  | 0.92  | 0.81  | 0.92  | 0.94  | 0.95   |
| RMSE  | 0.08   | 0.05  | 0.04  | 0.07  | 0.06  | 0.06  | 0.08  | 0.05   |
| SSE   | 0.09   | 0.08  | 0.07  | 0.11  | 0.09  | 0.05  | 0.06  | 0.07   |
| Sigmoid $F(x) = 1/[1 + e^{(x-x_0)/(-a)}]^b$ |        |       |       |       |       |       |       |        |
| <i>a</i>                                    | 0.64   | 0.22  | 0.51  | 0.03  | 0.70  | 0.64  | 0.71  | 0.30   |
| <i>b</i>                                    | 0.32   | 0.19  | 0.41  | 0.03  | 0.19  | 0.12  | 0.27  | 0.29   |
| $x_0$                                       | 5.36   | 1.86  | 5.07  | 3.23  | 5.57  | 10.22 | 9.45  | 4.26   |
| HC5   | 63.53  | 0.18  | 5.75  | 4.34  | 0.47  | 26.74 | 1.96  | 92.53  |
| $r^2$                                       | 0.96   | 0.96  | 0.99  | 0.99  | 0.99  | 0.93  | 0.99  | 0.99   |
| RMSE  | 0.07   | 0.02  | 0.03  | 0.04  | 0.04  | 0.08  | 0.03  | 0.04   |
| SSE   | 0.06   | 0.02  | 0.01  | 0.02  | 0.03  | 0.16  | 0.02  | 0.05   |
| Bootstrap                                   |        |       |       |       |       |       |       |        |
| HC5   | 92.63  | 0.23  | 8.69  | 7.36  | 0.62  | 36.32 | 3.05  | 135.23 |
| RMSE  | 0.006  | 0.002 | 0.005 | 0.006 | 0.005 | 0.002 | 0.007 | 0.007  |
| SSE   | 0.01   | 0.004 | 0.004 | 0.002 | 0.01  | 0.03  | 0.001 | 0.01   |
| Bootstrap regression                        |        |       |       |       |       |       |       |        |
| HC5   | 116.39 | 0.28  | 11.53 | 10.63 | 0.81  | 58.32 | 3.54  | 165.30 |
| RMSE  | 0.002  | 0.002 | 0.003 | 0.004 | 0.001 | 0.002 | 0.003 | 0.005  |
| SSE   | 0.004  | 0.004 | 0.006 | 0.008 | 0.004 | 0.004 | 0.005 | 0.006  |

The values are expressed as  $\mu\text{g/L}$ . Model parameters for parametric estimations are also presented

*SSE* error sum of squares, *RMSE* root mean square error

the least RMSE and SSE and greatest  $r^2$  was deemed to produce the most appropriate SSDs and HC5 values. The 95% confidence intervals of HC5 values were further generated with different methods (Aldenberg and Jaworska 2000; Grist et al. 2002).

### 2.3 Risk Assessment Procedure

The hazard quotient (HQ) approach was used to screen and characterize risks posed by metals and metalloids to aquatic species in Tai Lake. Utilizing this method is consistent with the guidelines of the technical guidance document on risk assessment of the European Union (EU 1996), wherein the MEC and hazard concentration were used to obtain a PNEC. The MECs of metals and metalloids in the water samples were then compared with PNEC values to calculate the HQ as

$$HQ = MEC / PNEC. \quad (1)$$

The PNEC is estimated by dividing the HC5 values by an uncertainty factor (UF),

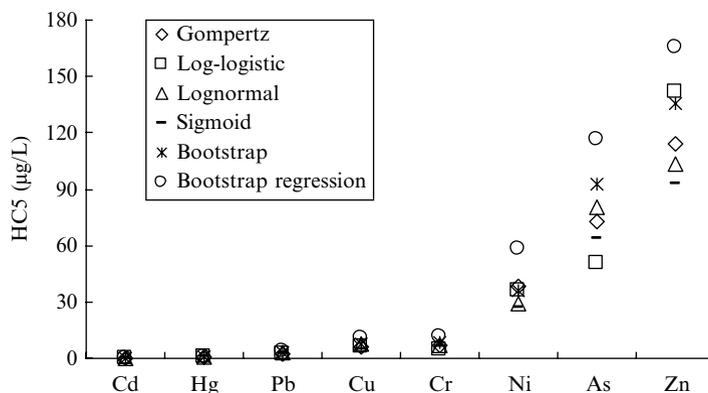
$$PNEC = HC5 / UF. \quad (2)$$

The UF value was set as 1 in this study, since the collected toxicity data were adequate to cover most of trophic levels of aquatic species (EU 1996). If the  $HQ \geq 1$ , a threshold for some degree of effect has been exceeded; values of  $0.1 \leq HQ < 1$  indicate that a medium risk is probable; and  $0.01 \leq HQ < 0.1$  indicate a low risk (Sanchez-Bayo et al. 2002).

## 3 SSD Construction and Model Comparison

### 3.1 Hazardous Concentration (HC5)

Profiles of estimated HC5 values and variables involved in the six approaches are shown in Table 2. The results of HC5 derived via six approaches were of the same order of magnitude. However, HC5 values obtained by the use of bootstrap or bootstrap regression were generally greater than those derived by using the parametric approach (Tukey's test in one-way ANOVA,  $F=525$ ,  $DF=5, 42$ ,  $P<0.001$ ). For instance, the HC5 value for Zn was 165.30  $\mu\text{g/L}$  when derived by the use of the bootstrap regression, whereas this value was 92.53  $\mu\text{g/L}$  when fitted to the log-logistic distribution. Based on overall estimates derived by the use of the various approaches, the order of decreasing toxicity of the eight elements tested was  $Zn < As < Ni < Cr < Cu < Pb < Hg < Cd$  (Fig. 2). These results are consistent with the toxicity study results on specific species with metals and metalloids (USEPA 1996).

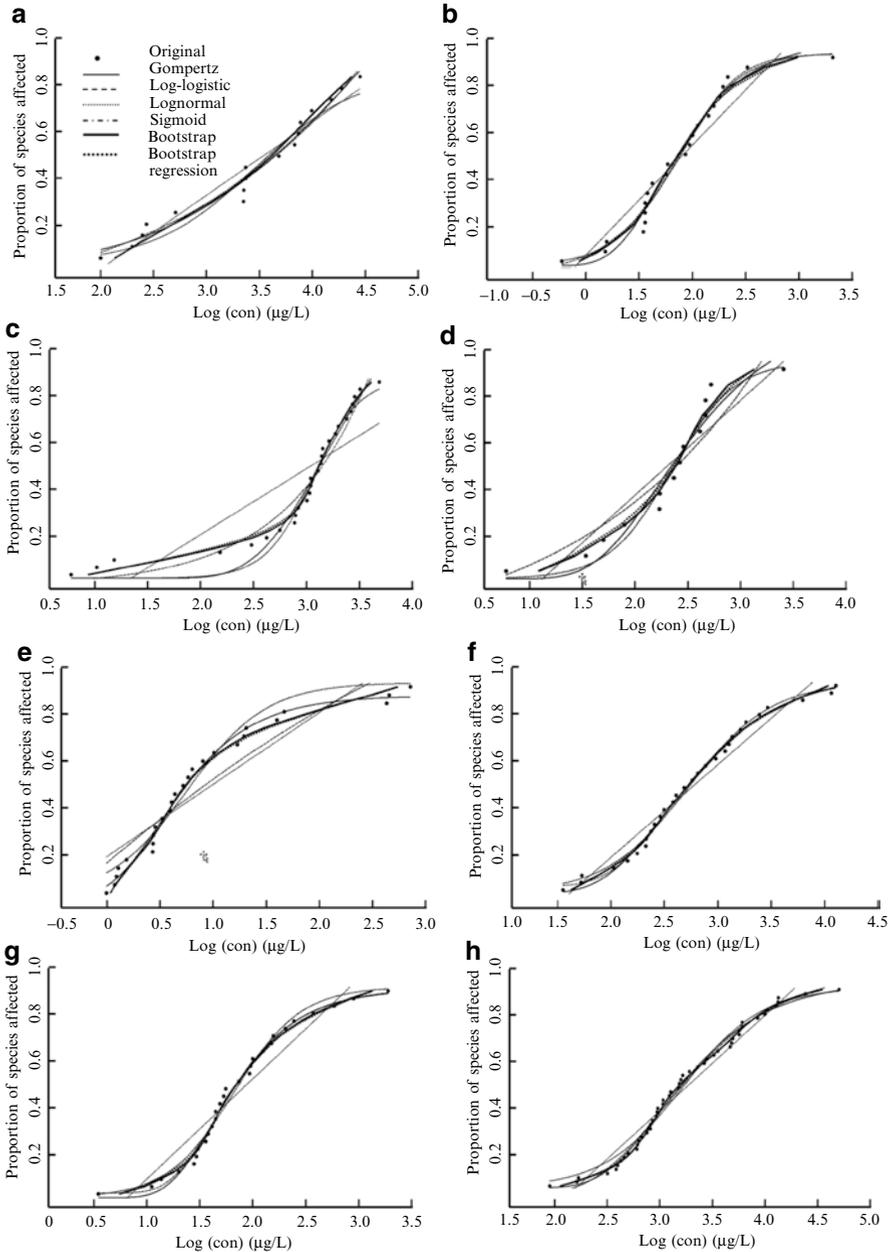


**Fig. 2** Comparison of HC5 values for metals and metalloids calculated by parametric and nonparametric approaches

HC5 values, derived from our review of available toxicity data, were compared with those published by the USEPA (1985, 1999). As an example of this comparison, HC5 values for Cd for China were in the range of 0.175–0.278  $\mu\text{g/L}$ , while the USEPA determined this value to be 0.25  $\mu\text{g/L}$ . Similar comparative results were observed for the five other metals evaluated (e.g., Cr, Hg, Ni, Pb, and Zn). In contrast, the HC5 values for As and Cu, published by the USEPA, were out of the range of those derived by using different approaches in this study. For example, the maximum HC5 value derived for As for China was 116.39  $\mu\text{g/L}$ , which was less than the value published by the USEPA. Notwithstanding, the difference between HC5 values derived in this study for China and those published by the USEPA was reasonable, probably for two reasons. First, the freshwater ecosystems for the two countries are located on different continents. For instance, the Great Lakes in the United States are quite different from freshwater aquatic systems present in China, featuring different geographical conditions and different populations of aquatic life (Rausina et al. 2002). Second, we used different analytical approaches than did the EPA in deriving HC5 values. Specifically, USEPA generally used derivation methods that depended on the four most sensitive genera (Meng and Wu 2010), whereas we derived values by analyzing the relationship between toxicity values of tested species and their corresponding cumulative probabilities. In addition, differences in target populations and their relative contributions to the aquatic ecological system also have been responsible for differences, as well (Wu et al. 2012).

### 3.2 Comparison of Approaches

SSDs derived by the use of the bootstrap, bootstrap regression, or conventional approaches were compared (Fig. 3a–h). In general, results obtained by using bootstrap or bootstrap regression followed the empirical data points exactly, whereas



**Fig. 3** Illustration of the SSDs derived by applying different approaches. (a) As ( $n=17$ ); (b) Cd ( $n=22$ ); (c) Cr ( $n=27$ ); (d) Cu ( $n=14$ ); (e) Hg ( $n=26$ ); (f) Ni ( $n=29$ ); (g) Pb ( $n=28$ ); (h) Zn ( $n=49$ ). Legends of (b–h) are referred in (a)

some curves derived by using other methods deviated from these points. For example, the curve fitted by using the sigmoid distribution (Fig. 3c) significantly deviated from the original data. In addition, the lower tail failed to exactly follow the raw data, although the data for Cr were generally well fitted by parametric approaches such as the log-logistic distribution (Fig. 3c). Consequently, the approaches shown in Fig. 3c, d are obviously not perfectly fitted results, since the first 5% of data on the curve could directly affect the HC5 values.

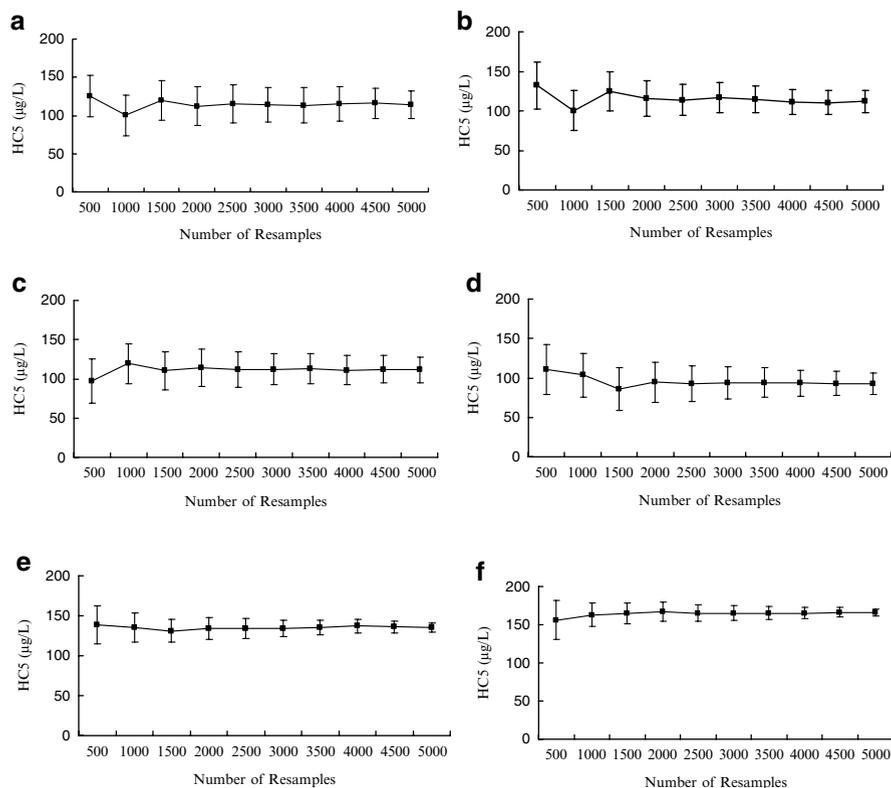
To compare the applicability of the bootstrap and conventional approaches for deriving an HC5 in SSDs, the SSE and RMSE values were calculated (Table 2) (Willmott et al. 1985; Moriasi et al. 2007). The RMSE values in the nonparametric estimates, bootstrap and bootstrap regression, were less than those observed in the parametric estimates. The nonparametric bootstrap approaches (Fig. 3e, f) fit the toxicity data better than the parametric approaches, where various frequency distributions were assumed (Fig. 3a–d).

Relationships between the variation of HC5 and the number of iterations during computational processes of parametric and nonparametric approaches are shown in Fig. 4a–f. The nonparametric processes (Fig. 4e, f) converged more quickly to a sufficiently small value of RSME, after iterations (700) than those conducted by the parametric approaches (2,000) (Fig. 4a–d) (Grist et al. 2002; Wang et al. 2008). Nonparametric approaches were superior (in convergence) to parametric curve-fitting methods during the computational processes (Townsend et al. 2007). In addition, the range of variation in HC5 values estimated by nonparametric methods was also narrower than that generated by parametric approaches. For instance, HC5 values for Zn estimated by the Gompertz distribution ranged 89.4–158.5  $\mu\text{g/L}$ , which was wider than the results conducted by the bootstrap regression with a range of 137.8–167.1  $\mu\text{g/L}$ . Bootstrap methods were generally more stable than those developed by the use of the parametric approaches.

### 3.3 Species Sensitivity

The SSDs used to derive HC5 showed that there was variability in species sensitivity. Compared with other taxa, aquatic plants showed a relatively wide range in sensitivities to all eight metallic elements. For instance, *Chlorella* sp. were generally sensitive to the effects of Cd, Cr, Cu, Hg, and Zn (Fig. 5b–e, h), while they were less sensitive to As and were tolerant to Pb. There was a range in tolerances of the angiosperm, *Lemna minor*. This species showed toxic effects when exposed to Cd and Zn (Fig. 5b, h) but was less sensitive to Cu and Hg (Fig. 5d, e).

Fishes were differentially sensitive to the toxicity of the elements studied. For example, the zebra fish (*Danio rerio*) was sensitive to Hg, Ni, and Pb (Fig. 5f, g), was moderately sensitive to As and Cd (Fig. 5a, b), and was tolerant of Zn (Fig. 5a–h). In contrast, the walking catfish (*Clarias gariepinus*) was tolerant to almost all of the polluting chemicals, especially Cu, Hg, and Ni (Fig. 5d, e, h).



**Fig. 4** Relationship between variation of HC5 of Zn and iterations made by different approaches ( $n=49$ ). (a) Gompertz; (b) log-logistic; (c) lognormal; (d) sigmoid; (e) bootstrap; (f) bootstrap regression. The *solid lines* indicate average HC5 values estimated by different approaches (for 500 iterations of simulation), and the *vertical bars* represent the associated standard deviations

Compared to other taxa, most species of zooplankton were relatively sensitive to the effects of all chemical treatments evaluated. Among all selected species, the model organism, *Daphnia magna*, was the most sensitive to As treatments (Fig. 5a), the third most sensitive to Cd and Cr (Fig. 5b, c) treatments, and was sensitive to Hg and Pb (Fig. 5e, g). This sensitivity of *D. magna* was consistent with the toxic test results in a previous relevant study (OECD 2011).

Macroinvertebrates were sensitive to most selected chemicals among species used to compile the SSDs. For instance, *Gammarus pulex* was the most sensitive species to Pb and the second most sensitive to As (Fig. 5a, g). Mollusks were moderately sensitive to most of the metals and metalloids such as *Mytilus edulis* and *Lamellidens marginalis* exposed to Hg (Fig. 5e) and *Dreissena polymorpha* exposed to Ni (Fig. 5f). Mollusks are suitable for both bio-monitoring and hazard and risk assessment (Borcherding and Volpers 1994; Salánki et al. 2003).



## 4 Risk Assessments

### 4.1 Measured Exposure Concentrations

Arithmetic mean concentrations of eight metals and metalloids to which aquatic species are exposed were measured in the 40 sites of Tai Lake (Table 3). The arithmetic mean values, rather than geometric mean values, were used for risk assessments, since concentrations had little variability (Yin and Fan 2011; Zhang et al. 2012). According to the *China Environmental Quality Standards for Surface Water* (GB3838-2002), the MECs of three metals and metalloids, such as As, Cd, and Hg, were less than the Class I regulation level, and the MECs for the other metals (i.e., Cr, Cu, and Zn) belong to the Class II levels, whereas Pb did not meet the requirements of the Class II level. Compared with the *China Standards for Irrigation Water Quality* (GB5084-2005) and *China Water Quality Standard for Fisheries* (GB11607-89), all metals and metalloids met the requirements except Cu. This indicated that most of the metals and metalloids fulfilled the requirements for employing lake water for uses such as irrigation and fisheries. However, the exposure concentrations of metals and metalloids in Tai Lake were higher than those that existed in a similar lake: Chaohu Lake (Tong et al. 2006). The main reason for this difference was the high industrial and agricultural discharge from Wuxi, Changzhou, and Suzhou that takes place around Tai Lake.

### 4.2 Correlation Analysis

A correlation analysis (Table 4) showed that there was a significant relationship among these metals, and this indicated that they emanated from sources that had

**Table 3** Comparison of values of MEC for metals and metalloids found in Tai Lake, and water quality standards of China from different sources

| Metals and metalloids | MEC ( $\mu\text{g/L}$ ) |                 |        | Environmental quality standards for surface water ( $\mu\text{g/L}$ ) |          | Standards for irrigation water quality ( $\mu\text{g/L}$ ) | Water quality standard for fisheries ( $\mu\text{g/L}$ ) |
|-----------------------|-------------------------|-----------------|--------|---|----------|--|--|
|                       | Range                   | Arithmetic mean | SD     | Class I   | Class II |  |  |
| As                    | 0.67–12.06              | 4.52            | 1.76   | 50  | 50       | 50   | 50   |
| Cd                    | 0.76–1.12               | 0.85            | 0.05   | 1   | 5        | 10   | 5  |
| Cr                    | 31.76–75.50             | 40.04           | 5.6    | 10  | 50       | 100  | 100  |
| Cu                    | 2.40–170.70             | 18.97           | 21.2   | 10  | 1,000    | 500  | 10   |
| Hg                    | 0.001–0.246             | 0.0048          | 0.004  | 0.05  | 0.05     | 1  | 0.5  |
| Ni                    | 16.60–30.91             | 19.61           | 1.86   | –   | –        | –  | 50   |
| Pb                    | 9.89–29.81              | 16.9            | 3.34   | 10  | 10       | 200  | 50   |
| Zn                    | 17.66–1,246             | 70.26           | 154.33 | 50  | 1,000    | 2,000  | 100  |

–, no data available; MEC, measured exposure concentration

**Table 4** Correlation coefficients between eight metals and metalloids

|    | As     | Cd     | Cu     | Cr      | Hg     | Ni     | Pb    | Zn    |
|----|--------|--------|--------|---------|--------|--------|-------|-------|
| As | 1.000  |        |        |         |        |        |       |       |
| Cd | 0.134  | 1.000  |        |         |        |        |       |       |
| Cu | 0.005  | 0.301  | 1.000  |         |        |        |       |       |
| Cr | 0.319  | 0.562* | -0.091 | 1.000   |        |        |       |       |
| Hg | -0.072 | -0.276 | -0.062 | -0.183  | 1.000  |        |       |       |
| Ni | 0.292  | 0.448  | -0.032 | 0.714*  | -0.399 | 1.000  |       |       |
| Pb | 0.293  | 0.254  | -0.046 | 0.306   | -0.034 | 0.187  | 1.000 |       |
| Zn | 0.264  | 0.624* | -0.068 | 0.873** | -0.151 | 0.544* | 0.306 | 1.000 |

\*Significant at the 0.05 level (two tailed)

\*\*Significant at the 0.01 level under the null hypothesis of  $\rho=0$

**Table 5** Hazard quotients of metals and metalloids to aquatic species in the Tai Lake calculated by HC5 values derived from SSDs based on six different approaches

| Metals and metalloids | As     | Cd      | Cr      | Cu      | Hg    | Ni     | Pb      | Zn     |
|-----------------------|--------|---------|---------|---------|-------|--------|---------|--------|
| Approaches            |        |         |         |         |       |        |         |        |
| Gompertz              | 0.062  | 4.722** | 5.976** | 3.237** | 0.008 | 0.507* | 7.161** | 0.615* |
| Log-logistic          | 0.107* | 3.696** | 9.059** | 3.221** | 0.009 | 0.544* | 7.578** | 0.628* |
| Lognormal             | 0.056  | 5.313** | 5.317** | 2.769** | 0.009 | 0.682* | 5.748** | 0.677* |
| Sigmoid               | 0.071  | 4.722** | 6.963** | 4.371** | 0.01  | 0.73*  | 8.622** | 0.759* |
| Bootstrap             | 0.0049 | 3.696** | 4.608** | 2.577** | 0.008 | 0.540* | 5.541** | 0.520* |
| Bootstrap regression  | 0.039  | 3.036** | 3.473** | 1.785** | 0.006 | 0.336* | 4.774** | 0.425* |

Asterisk number indicates the risk levels of metals and metalloids: low risk (none), medium risk (\*), and high risk (\*\*)

similar and related anthropogenic activities. Rather high correlations were found between Cd and Zn (0.624), Cr and Ni (0.714), and Cr and Zn (0.873). This led us to believe that effluents from neighboring industries and municipal sewage might contribute to substantial loads of metals–metalloids to the rivers flowing from city and rural areas. For example, Cd is usually regarded as deriving from anthropogenic-sourced wastewater and fertilizers, or pesticides, whereas Cr, Ni, and Zn are usually connected with printing or electroplating industry discharges (Li et al. 2009).

### 4.3 Hazard Quotients

The PNEC value is equal to the HC5 value, since the UF was set as 1 in this study (EU 1996). The hazard quotients can be directly derived by dividing the MEC and HC5 (1 and 2). For each HC5 value calculated from SSDs using different approaches, we obtained the corresponding HQ value for assessing the risk of metals and metalloids (Table 5). Generally, the decreasing order of the HQ values for the eight

elements was as follows:  $Hg < As < Ni < Zn < Cu < Cd < Pb < Cr$ . The more toxic elements, Cr, Pb, and Cd, exhibited greater risks. This is reasonable considering that these three metals have both greater toxic potency and greater rates of discharge. Many factories exist around Tai Lake, including printing houses and electroplating factories, and thereby serve as sources of these metallic contaminants. From our analysis, risks of Cu, Zn, and Ni were somewhat in the middle range, although their human health toxicities are not that great. Of course, these are also essential dietary metals for humans. The last two elements, As and Hg, showed the least risk to aquatic species. This is mainly due to their lesser natural concentrations, although they are commonly thought of as being among the most toxic metals.

Applying different SSD approaches to the data produced different HC5 values for protecting aquatic species from metals and metalloids. Moreover, utilizing different approaches affected the hazard quotients and risk levels for aquatic species. For instance, the HQ for As, calculated by HC5 through bootstrap regression, was 0.039 at the lesser level of risk, whereas it was 0.107 at the medium level of risk when conducted by a log-logistic distribution. Consequently, what model is selected to treat the data is not only important when deriving WQC values but also a key issue when assessing the risk of water pollutants.

## 5 Discussion

### 5.1 Evaluation of Approaches

When constructing SSDs, one limitation of conventional parametric methodologies is that no single frequency distribution adequately fits all of the available data (Grist et al. 2006). In particular, the accuracy and precision are poor when sample sizes are very small (Moore and Caux 1997). This effect can be seen from curves fitted with the standard log-logistic and sigmoid distributions for Cr (Fig. 3c). In such cases, the HC5 obtained are distorted. Because bootstrapping does not require designation of a particular statistical distribution of chemical effects on species assemblages, it could be an alternative tool to deal with this limitation. Bootstrapping requires a precondition that the empirical distribution of endpoint values could truly represent the real distribution of the source data in the world (Efron and Tibshirani 1993; Grist et al. 2002). Advantages and disadvantages of both conventional parametric and bootstrap approaches were addressed by Grist et al. (2002), when the bootstrap regression approach was first introduced to construct SSDs for ecological risk assessments. The bootstrap approach does not force a distribution onto data, but it is a relatively data-intensive technique that completely ignores a priori information about distributions of biological responses. In contrast, the parametric approaches most frequently used in deriving SSDs for ecological risk assessment generally require simple computations but make more demanding assumptions about the distribution of data.

## 5.2 Selection of Approaches

Using toxicity data of representative aquatic species and typical water contaminants in China, a comparison of six approaches showed that nonparametric methods based on bootstrapping were statistically superior to the parametric curve-fitting approaches. These results were generally consistent with previous comparisons of multiple approaches that have been applied to derive hazardous concentrations of contaminants in water. For instance, Wheeler et al. (2002) applied four approaches (viz., log-logistic, lognormal, bootstrap, and bootstrap regression) to construct SSDs based on acute lethality of Ni and Cd to saltwater organisms. They found that curves generated by bootstrap and bootstrap regression best matched toxicity data among the approaches. The superiority of bootstrap methods was also reported when developing SSDs on the toxicity of organochlorine pesticides (Wang et al. 2008). These results suggested that bootstrap methods showed promising applications for protecting sensitive species than conventional parametric fitting methods. However, it is still too early to conclude that the bootstrap is the best model to simulate SSDs for all circumstances. Like HC5 values, the applicability of a particular model could be affected by several factors, including available data amounts, species composition, data selected, chemical toxicity, and geographical characteristics.

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 relate to their geographic distribution (Brock et al. 2006). For instance, the most common fishes in China are species of Cyprinidae, while in North America it is Salmonidae. Moreover, because of limited toxicity data from literatures, the species used in this study cannot represent all common aquatic organisms in the natural aquatic environment of China. A more sufficient set of toxicity data, covering as many as possible representative species, will be used in further studies. Applications of the same model and metal on chronic toxicity data would be different from those on acute toxicity data. One example is developing SSDs for acute and chronic toxicity of Zn to Chinese species by using parametric fitting methods (Wu et al. 2011). The exponential distribution ( $F(x) = 1 - \exp(-\lambda x)$ ,  $x > 0$ ) gave the best fit to the acute data, while the sigmoid distribution was superior to other methods for fitting the chronic data.

Considering both the advantages and disadvantages of the approaches investigated in this study, if there are sufficient data and if parametric approaches fit the data well, they should be chosen for because of their computational simplicity (Wheeler et al. 2002). However, if the parametric descriptors fail to fit the toxicity data, in which species number is over than 20, the standard bootstrap methods should be used; otherwise, if the data number is less than 20, the bootstrap regression is a better choice by stochastically inserting values.

### ***5.3 Proportion of Species to Be Protected***

Values for HC5 derived in this study indicate that if the concentration of a certain pollutant is less than the HC5, more than 95% of aquatic species that are chronically exposed would not be adversely affected (Aldenberg and Jaworska 2000). The species proportion to be protected from pollutant chemicals involved in SSDs would be a key issue for establishing water quality criteria. The goal of the WQC is to ensure that toxicants appearing in water and sediment do not adversely affect all or most populations of species in a particular ecosystem and do not impair the overall structure or function of the ecosystem. Although the use of the fifth centile of the biological species is arbitrary, it is generally applied in slightly to moderately disturbed areas and is widely used. A 99% level of protection is appropriate in areas of greater ecological value or where there are concerns about bioaccumulation or toxicity to endangered species. A lesser level of protection might be appropriate, at least as an interim measure, in more disturbed areas. Consequently, the level adopted varies among countries or geographies. For instance, Canadian guidelines aim to protect 100% of species everywhere from long-term exposure (CCME 1999), whereas Australia (ANZECC and ARMCANZ 2000), the European Union (European Commission 2000), and the United States (USEPA 1986) seek to protect a percentage of species, usually 95%, sometimes 99% (pristine areas) or 80% (heavily modified ecosystems).

### ***5.4 HQ for Risk Assessment***

HQ values were effectively used for screening-level ecological risk assessments for Tai Lake. However, the results of ecological risk assessment are conservative and preliminary considering several factors such as sampling frequency, available toxicity data, and environmental conditions. First, water samples were only collected over a short period in September of 2009. To better reflect and characterize the status of these metals for the long term, seasonal sampling of metal content is needed. Second, limited numbers of metals and metalloids and exposed species were addressed. Inclusion of additional metals or organic pollutants may change the potential risk to aquatic species. Third, exposure concentrations are dynamic in the context of environmental factors such as temperature, pH, and dissolved oxygen. In addition, the species composition in the assessed target water body is variable from seasonal change. Such dynamic changes in the community need to be considered in future studies.

## **6 Summary**

Both nonparametric and parametric approaches were used to construct SSDs for use in ecological risk assessments. Based on toxicity to representative aquatic species and typical water contaminants of metals and metalloids in China,

nonparametric methods based on the bootstrap were statistically superior to the parametric curve-fitting approaches. Knowing what the SSDs for each targeted species are might help in selecting efficient indicator species to use for water quality monitoring. The species evaluated herein showed sensitivity variations to different chemical treatments that were used in constructing the SSDs. For example, *D. magna* was more sensitive than most species to most chemical treatments, whereas *D. rerio* was sensitive to Hg and Pb but was tolerant to Zn.

HC5 values, derived for the pollutants in this study for protecting Chinese species, differed from those published by the USEPA. Such differences may result from differences in geographical conditions and biota between China and the United States. Thus, the degree of protection desired for aquatic organisms should be formulated to fit local conditions. For approach selection, we recommend all approaches be considered and the most suitable approaches chosen. The selection should be based on the practical information needs of the researcher (viz., species composition, species sensitivity, and geological characteristics of aquatic habitats), since risk assessments usually are focused on certain substances, species, or monitoring sites.

We used Tai Lake as a typical freshwater lake in China to assess the risk of metals and metalloids to the aquatic species. We calculated hazard quotients for the metals and metalloids that were found in the water of this lake. Results indicated the decreasing ecological risk of these contaminants in the following order: Hg < As < Ni < Zn < Cu < Cd < Pb < Cr. From the methodological perspective, six SSD approaches used delivered different WQC values and affected the risk assessment results of the metals and metalloids to aquatic species. Based on the MEC and HC5 derived from SSDs by nonparametric and parametric approaches together, the risk levels of metals and metalloids were characterized from their hazard quotients as being high risk (Cr, Pb, Cd, and Cu), medium risk (Zn and Ni), or low risk (As and Hg).

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## References

- Aldenberg T, Jaworska JS (2000) Uncertainty of the hazardous concentration and fraction affected for normal species sensitivity distributions. *Ecotoxicol Environ Saf* 46:1–18
- Aldenberg T, Slob W (1993) Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. *Ecotoxicol Environ Saf* 25:48–63

- ANZECC, ARMCANZ (2000) Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra
- Balk F, Okkerman PC, Dogger JW (1995) Guidance document for aquatic effects assessment. Organization for Economic Co-operation and Development (OECD), Paris
- Batley GE (2012) "Heavy metal"—a useful term. *Integr Environ Assess Manag* 8:215
- Borcherding J, Volpers M (1994) The "Dreissena-monitor". First results on the application of this biological early warning system in the continuous monitoring of water quality. *Water Sci Technol* 29:199–201
- Brock TCM, Arts GHP, Maltby L, Van den Brink PJ (2006) Aquatic risks of pesticides, ecological protection goals, and common aims in European Union legislation. *Integr Environ Assess Manag* 2:20–46
- Calow P (1996) Variability: noise or information in ecotoxicology? *Environ Toxicol Pharmacol* 2:121–123
- Campbell P, Stokes P (1985) Acidification and toxicity of metals to aquatic biota. *Can J Fish Aquat Sci* 42:2034–2049
- Campbell KR, Bartell SM, Shaw JL (2000) Characterizing aquatic ecological risks from pesticides using a diquat dibromide case study. II. Approaches using quotients and distributions. *Environ Toxicol Chem* 19:760–774
- CCME (1999) Canadian environmental quality guidelines. Canadian Council of Ministers of the Environment, Winnipeg
- Chapman PM (2012) "Heavy metal"—cacophony, not symphony. *Integr Environ Assess Manag* 8:216
- R Development Core Team (2011) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL <http://www.R-project.org/>
- Duffus JH (2002) "Heavy metals" a meaningless term? *Pure Appl Chem* 74:793–807
- ECB (2003) Technical guidance document on risk assessment—Part II. Technical report. Institute for Health and Consumer Protection, Ispra, Italy
- Efron B, Tibshirani R (1993) An introduction to the bootstrap. Chapman & Hall, Boca Raton, FL
- EU (1996) Technical guidance document on risk assessment in support of council directive 93/67/EEC on risk assessment for new notified substances, commission regulation (EC) 1488/94 on risk assessment for existing substances
- European Commission (2000) Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy. *OJEC L327*:1–72
- Forbes TL, Forbes VE (1993) A critique of the use of distribution-based extrapolation models in ecotoxicology. *Funct Ecol* 7:249–254
- Giesy JP, Solomon KR, Coats JR, Dixon KR, Giddings JM, Kenaga EE (1999) Chlorpyrifos: ecological risk assessment in North American aquatic environments. *Rev Environ Contam Toxicol* 160:1–129
- Grist EPM, Leung KMY, Wheeler JR, Crane M (2002) Better bootstrap estimation of hazardous concentration thresholds for aquatic assemblages. *Environ Toxicol Chem* 21:1515–1524
- Grist EPM, O'Hagan A, Crane M, Sorokin N, Sims I, Whitehouse P (2006) Bayesian and time-independent species sensitivity distributions for risk assessment of chemicals. *Environ Sci Technol* 40:395–401
- Jagoe R, Newman MC (1997) Bootstrap estimation of community NOEC values. *Ecotoxicology* 6:293–306
- Klimisch H, Andreae M, Tillmann U (1997) A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data. *Regul Toxicol Pharmacol* 25:1–5
- Li JL, He M, Han W, Gu YF (2009) Analysis and assessment on heavy metal sources in the coastal soils developed from alluvial deposits using multivariate statistical methods. *J Hazard Mater* 164:976–981
- Mance G (1987) Pollution threat of heavy metals in aquatic environments. Springer, New York
- Marchant C, Leiva V, Cavieres MF, Sanhueza A (2013) Statistical distributions with application to PM10 in Santiago, Chile. *Rev Environ Contam Toxicol* 223:1–31

- Meng W, Wu FC (2010) Introduction of water quality criteria theory and methodology (in Chinese). Science Press, Beijing
- Moore DRJ, Caux PY (1997) Estimating low toxic effects. *Environ Toxicol Chem* 16:794–801
- Moriassi D, Arnold J, Van Liew M, Bingner R, Harmel R, Veith T (2007) Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. *Trans ASABE* 50:885–900
- Newman MC, Ownby DR, Mezin LCA, Powell DC, Christensen TRL, Lerberg SB, Anderson BA (2000) Applying species sensitivity distributions in ecological risk assessment: assumptions of distribution type and sufficient numbers of species. *Environ Toxicol Chem* 19:508–515
- Nogawa K, Kido T (1993) Biological monitoring of cadmium exposure in itai-itai disease epidemiology. *Int Arch Occup Environ Health* 65:43–46
- OECD (2011) Proposal for updated guideline 211 *Daphnia magna* reproduction test. Organization for Economic Co-operation and Development, Paris
- Pennington DW (2003) Extrapolating ecotoxicological measures from small data sets. *Ecotoxicol Environ Saf* 56:238–250
- Posthuma L, Suter GW, Traas TP (2002) Species sensitivity distributions in ecotoxicology. CRC Press, Boca Raton, FL
- Power M, McCarty LS (1997) Fallacies in ecological risk assessment practices. *Environ Sci Technol* 31:370A–375A
- Rausina GA, Wong DCL, Raymon Arnold W, Mancini ER, Steen AE (2002) Toxicity of methyl tert-butyl ether to marine organisms: ambient water quality criteria calculation. *Chemosphere* 47:525–534
- RIVM (2007) Guidance document on deriving environmental risk limits in The Netherlands, report 601501012. National Institute of Public Health and the Environment, Bilthoven, The Netherlands
- Salánki J, Farkas A, Kamardina T, Rózsa KS (2003) Molluscs in biological monitoring of water quality. *Toxicol Lett* 140:403–410
- Sanchez-Bayo F, Baskaran S, Kennedy IR (2002) Ecological relative risk (EcoRR): another approach for risk assessment of pesticides in agriculture. *Agric Ecosyst Environ* 91:37–57
- Shao Q (2000) Estimation for hazardous concentrations based on NOEC toxicity data: an alternative approach. *Environmetrics* 11:583–595
- Shaw WHR, Grushkin B (1957) The toxicity of metal ions to aquatic organisms. *Arch Biochem Biophys* 67:447–452
- Solomon KR, Baker DB, Richards RP, Dixon KR, Klaine SJ, La Point TW, Kendall RJ, Weisskopf CP, Giddings JM, Giesy JP, Hall LW, Williams WM (1996) Ecological risk assessment of atrazine in North American surface waters. *Environ Toxicol Chem* 15:31–76
- Solomon KR, Giesy JP, Jones P (2000) Probabilistic risk assessment of agrochemicals in the environment. *Crop Prot* 19:649–655
- SPSS Inc. (2008) SPSS statistics for windows, version 17.0. SPSS Inc., Chicago, IL
- Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, Brungs WA (1985) Guidelines for deriving numeric national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049. National Technical Information Services, Springfield, VA
- TenBrook PL, Palumbo AJ, Fojut TL, Hann P, Karkoski J, Tjeerdema RS (2010) The University of California-Davis methodology for deriving aquatic life pesticide water quality criteria. In: Whitacre DM (ed) Reviews of environmental contamination and toxicology, vol 209. Springer Science + Business Media, LLC, New York, pp 1–155
- Tong JH, Huang XM, Chen Y (2006) Evaluation of contamination of heavy metal in Chaohu lake (in Chinese). *J Anhui Agric Sci* 17:4373–4374
- Townsend PA, Papeş M, Eaton M (2007) Transferability and model evaluation in ecological niche modeling: a comparison of GARP and Maxent. *Ecography* 30:550–560
- Tsushima K, Naito W, Kamo M (2010) Assessing ecological risk of zinc in Japan using organism- and population-level species sensitivity distributions. *Chemosphere* 80:563–569
- USEPA (1968) Report of the subcommittee of water quality criteria. Technical report. US Department of the Interior, Washington, DC

- USEPA (1976) Quality criteria for water. EPA 440/9-76/023. Office of Water Planning and Standards, Washington, DC
- USEPA (1985) Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses, PB-85-227049. US Environmental Protection Agency, National Technical Information Service, Springfield, VA
- USEPA (1986) Quality criteria for water. EPA-440/5-86-001. Office of Water Regulations and Standards, Washington, DC
- USEPA (1996) Water quality criteria documents for the protection of aquatic life in ambient water: 1995 updates. EPA-820-B-96-001. Office of Water, Washington, DC
- USEPA (1999) National recommended water quality criteria-correction. EPA-822-Z-99-001. Office of Water, Washington, DC
- USEPA (2002) National recommended water-quality criteria: 2002. EPA-822-R-02-047. Office of Water, Washington, DC
- USEPA (2004) National recommended water quality criteria. Office of Water, Office of Science and Technology, Washington, DC
- USEPA (2009) National recommended water quality criteria. Office of Water, Washington, DC
- van Dam RA, Harford AJ, Warne MSJ (2012) Time to get off the fence: the need for definitive international guidance on statistical analysis of ecotoxicity data. *Integr Environ Assess Manag* 8:242–245
- van Sprang PA, Verdonck FAM, van Assche F, Regoli L, De Schampheleere KAC (2009) Environmental risk assessment of zinc in European freshwaters: a critical appraisal. *Sci Total Environ* 407:5373–5391
- van Straalen NM (2002) Threshold models for species sensitivity distributions applied to aquatic risk assessment for zinc. *Environ Toxicol Pharmacol* 11:167–172
- van Straalen NM, Denneman CAJ (1989) Ecotoxicological evaluation of soil quality criteria. *Ecotoxicol Environ Saf* 18:241–251
- Vardy DW, Tompsett AR, Sigurdson JL, Doering JA, Zhang X, Giesy JP, Hecker M (2011) Effects of subchronic exposure of early life stages of white sturgeon (*Acipenser transmontanus*) to copper, cadmium, and zinc. *Environ Toxicol Chem* 30:2497–2505
- Varian H (2005) Bootstrap tutorial. *Math J* 9:768–775
- Wagner C, Løkke H (1991) Estimation of ecotoxicological protection levels from NOEC toxicity data. *Water Res* 25:1237–1242
- Wang B, Yu G, Huang J, Hu H (2008) Development of species sensitivity distributions and estimation of HC5 of organochlorine pesticides with five statistical approaches. *Ecotoxicology* 17:716–724
- Wheeler JR, Grist EPM, Leung KMY, Morrill D, Crane M (2002) Species sensitivity distributions: data and model choice. *Mar Pollut Bull* 45:192–202
- WHO (2006) Guidelines for drinking water quality: incorporation 1st and 2nd addenda. Technical report, vol 1, 3rd edn. WHO, Geneva, recommendations
- Willmott CJ, Ackleson SG, Davis RE, Feddema JJ, Klink KM, Legates DR, O'Donnell J, Rowe CM (1985) Statistics for the evaluation and comparison of models. *J Geophys Res* 90: 8995–9005
- Wu FC, Meng W, Zhao XL, Li HX, Zhang RQ, Cao YJ, Liao HQ (2010) China embarking on development of its own national water quality criteria system. *Environ Sci Technol* 44: 7992–7993
- Wu FC, Feng CL, Cao YJ, Zhang RQ, Li HX, Liao HQ, Zhao XL (2011) Toxicity characteristic of zinc to freshwater biota and its water quality criteria (in Chinese). *Asian J Ecotoxicol* 6:367–382
- Wu FC, Feng CL, Zhang RQ, Li YS, Du DY (2012) Derivation of water quality criteria for representative water-body pollutants in China. *Sci China Earth Sci* 55:900–906
- Yin HY, Fan C (2011) Dynamics of reactive sulfide and its control on metal bioavailability and toxicity in metal-polluted sediments from Lake Taihu, China. *Arch Environ Contam Toxicol* 60:565–575
- Zhang Y, Hu X, Yu T (2012) Distribution and risk assessment of metals in sediments from Taihu Lake, China using multivariate statistics and multiple tools. *Bull Environ Contam Toxicol* 89:1009–1015