Environ Sci Pollut Res (2014) 21:12968–12978
DOI 10.1007/s11356-014-3156-5

RESEARCH ARTICLE

Weighted species sensitivity distribution method to derive site-specific quality criteria for copper in Tai Lake, China

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Received: 29 January 2014 / Accepted: 4 June 2014 / Published online: 2 July 2014

Abstract Tai Lake (Ch: *Taihu*), which is the largest lake in Jiangsu province, China, has been affected by human activities. As part of a concerted effort to improve water quality to protect the integrity of the Tai Lake ecosystem, a water quality criterion (WQC) was developed for copper (Cu) II. The acute WQC was based on 440 values for acute toxicity of Cu to 24 species from 6 phyla, 16 families, and 20 genera. In addition, 255 values for chronic toxicity of Cu to 10 species from 5 phyla, 8 families, and 9 genera were used to derive chronic WQC. Instead of using a traditional approach based species sensitivity distributions (SSD), a weighted species sensitivity distribution (WSSD) approach was used to calculate the cumulative probability based on endemic species to Tai Lake. Acute and chronic WQC developed by use of the WSSD were 5.3 and 3.7 μg Cu/L, respectively. While the WQC values were comparable to those of other countries, there were slight differences due to variability in species composition of different regions. The site-specific criteria indicated that the current standard set for surface water by the Chinese government might not be protective of aquatic organisms in Tai Lake.

Keywords Weighted species sensitivity distributions · Probabilistic · Asia · Model · Statistics

Introduction

Water quality criteria (WQC) are based on the concentration less than which no adverse effects would be expected for humans or wildlife for uses of water, such as drinking, recreation, aquaculture, irrigation of agriculture, and use by industries. Thus, WQC are the foundation for the protection of environments by agencies that monitor and manage the quality of surface waters (Meng et al. 2006). In China, WQC have been established for some chemicals, but they are mainly derived from environmental quality standards or criteria that have been developed by other jurisdictions (Jin et al. 2014; Liu et al. 2014). However, due to differences between hydrographic conditions and species in China and those in other countries, these WQC might be overprotective or underprotective of endemic aquatic species (Wu et al. 2010). To minimize these uncertainties, in 2008, the Major State Basic Research Development Program and the National Major Project of Science and Technology Ministry of China were initiated. Therefore, China is now building its own WQC system "de novo" (Feng et al. 2012) based on its natural features and magnitude of economic development, to protect the ecosystem, human health and manage aquatic environments (Zhou et al. 2007).

More economically developed countries, such as the Netherlands, Australia, Canada, and the USA, and international organizations, such as the European Union (EU) and the World Health Organization (WHO), have issued guidelines to derive WQC. Despite different methods used, the principles

Responsible editor: Thomas Braunbeck

Electronic supplementary material The online version of this article (doi:10.1007/s11356-014-3156-5) contains supplementary material, which is available to authorized users.

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applied by these jurisdictions are similar in that they are based on empirical data for toxic potencies of chemicals to various aquatic organisms and uncertainty factors (Suter and Cormier 2008). The two methods that have been used are that of assessment factors (AF) (EMEA 2004a, b) and species sensitivity distributions (SSD) (Kooijman 1987). Currently, the SSD approach is increasingly used and has been applied to develop WQC for China (Xing et al. 2012, 2014).

A SSD is a cumulative probability distribution (Posthuma et al. 2002). Based on this function, a specific concentration, referred to as the hazardous concentration (HC) can be derived that relates to a probability of a fraction p(%) of species which would exceed the threshold for an endpoint-specific effect. Among the HCs, the HC_5 and HC_{10} are most frequently used to establish criteria for protection of integrity of aquatic communities. Theoretically, these two values would ensure that 95 and 90 % of aquatic species would not be affected. However, this does not mean that 5 or 10 % of species in natural environments would be affected. In fact, due to mitigation of exposures in natural environments that result in lesser bioavailability than would occur under laboratory conditions, the HC_5 has been found to correspond to the no observed adverse effect concentration (NOAEC) based on multispecies, microcosms studies (Giesy et al. 1999).

The SSD approach also allows managers to determine which species are most likely to be affected so that potential key species or sentinel species can be identified and protected. However, three questions about methods based on SSD have been raised by Forbes and Forbes (1993) and Forbes and Calow (2002): First, should intra-species variation be considered in addition to toxicological data for individual species? Second, how should WQC account for differences in sensitivities among classes of organisms such as vertebrates, invertebrates, and algae? Third, which statistical method should be used to construct the distribution SSD and calculate the HC_5? It has been suggested by Duboudin et al. (2004) that there are 63 different ways to calculate the HC_5 from the same set of data. In addition, it has been found that choice of data (intra-species variation and proportions between taxonomic groups) has more effect on the value of HC_5 than statistical methods applied to fit the functions and that weight given to various taxonomic groups is the most important parameter (Xing et al. 2012). Therefore, weights given to the three primary categories (invertebrate, vertebrate, and algae) should be considered. As a result, the weighted species sensitivity distribution (WSSD) method has been developed to minimize shortcomings perceived in SSD approaches that do not incorporate weights applied taxonomic groups when calculating HC values (Kooijman 1987; Xing et al 2012).

Copper (Cu) is a metal contaminant in freshwaters of China and mainly enters the aquatic environment from atmospheric deposition, agricultural runoff, and industrial effluents. Also, copper sulfate has been used historically to control algal blooms and snails that are the intermediate hosts for schistosomiasis (Wu et al. 2011), which has resulted in Cu(II) in surface water. Although Cu is an essential trace element, excess concentrations can cause adverse effects on aquatic organisms (Wu et al. 2011). The current surface water quality standards (WQS) for copper are classified into five levels. Level I WQS for Cu is 10 μg Cu/L, while the standard for level II~V waters are 1,000 μg Cu/L (China EPA 2002). Since these standards might not be protective under all situations, the WQC for Cu on which the WQS are based was reassessed relative to the situation in Tai Lake in this study.

Methodology and data collection

Toxicological data collection and screening

Toxicological data of Cu to aquatic organisms were collected from the ECOTOX (HTTP://cfpub.epa.gov/ecotox/) database. This database contained information for fishes, insects, crustaceans, mollusks, algae, and amphibians. Copper sulfate ($CuSO_4$) and copper chloride ($CuCl_2$) were considered, and results were reported as Cu(II) ions. To be considered, data were screened strictly based on several criteria (Klimisch et al. 1997; Stephan et al. 1985; Wheeler et al. 2002):

1. All the toxicological experiments had to conform to the standard methods proscribed by China, the USA, or some international organization like OECD.
2. Have an explicit test endpoint, be of appropriate duration, and provide a complete description of the methods applied.
3. Unicellular organisms were not accepted for acute toxicity and the *Daphnia* sp. used in tests should be younger than 24 h; larvae of the family Chironomidae had to be less than 2 or 3 days of age.
4. Feeding was not allowed during exposures.
5. EC_{50} and LC_{50} were used as endpoints for acute toxicological data; 48-h EC_{50} or LC_{50} were selected as the acute toxicological endpoints for *Daphnia* or other cladocerans and Chironomidae larvae, while 96-h EC_{50} or LC_{50} were used for fish and other aquatic life (Stephan et al. 1985).
6. If the species mean acute value (SMAV) of an important species was less than its final acute value (FAV), the SMAV was used for that species.
7. No observed effect concentrations (NOEC) or lowest observed effect concentrations (LOEC) were used as the endpoints for chronic toxicological data. when there was a lack of chronic data, results from tests of at least 7-day duration with early life stages, such as embryos of fishes or an acute to chronic ratio was used (Wheeler et al. 2002). When there was more than one value for the same

endpoint and species, the geometric mean was used (Stephan et al. 1985).

8. When some toxicological data of the species were abnormal, for example, more than a magnitude than other data of the same species, test conditions, and method were checked (Klimisch et al. 1997). If they were absent, this data were excluded.

Target species

Target species used in this assessment were those naturally found in Tai Lake (Su 2011) (Fig. S1), including Chinese native species, as well as some species imported from other countries but widespread in China (Jin et al. 2012a, b; Xing et al. 2012, 2014). For example, the rainbow trout (*Oncorhynchus mykiss*), which is an exotic salmonid imported from Japan but now widespread in freshwaters of China, were also used as a surrogate for characteristics of Chinese freshwater ecosystem. By using species that are present in Tai Lake, it was hoped to be able to derive a more site-specific WQC.

Base on biodiversity of the Tai Lake ecosystem, various trophic levels and distributions of the toxicological data were considered, and 440 observations of acute toxicity for 24 species from 6 phyla, 16 families, and 20 genera were included in the data set. For the development of the chronic criterion, 255 data points for 10 species from 5 phyla, 8 families, and 9 genera were used. Species mean values, genus mean values, as well as individual data points for both acute and chronic exposures are presented (Tables 1 and 2).

Weighting coefficients

The SSD method (Kooijman 1987) has been widely used for deriving WQC in many jurisdictions, including the USA, Canada, Netherlands, and China. In this method, the distribution is first checked to determine if it could be described by the normal probability function and concentrations are log-transformed. Data points were then sorted from least to greatest and each point plotted in cumulative probability as a function of log concentration. Plotting positions were calculated (Eq. 1).

$$\text{Cumulative probability} = i/(n+1) \tag{1}$$

where i represents the rank of a species in the data series, and n is the total number of species examined (Hall et al. 1998; Schuler et al. 2008). SSD curves were constructed for acute and chronic values, respectively. The HC_5 was then interpolated from the SSD function (Figs. 1 and 2).

In developing the SSD, the discriminatory power of the resulting cumulative frequency distribution is constrained by the number of species included in the analysis. For instance if 100 discrete data points (species) were used, the power of discrimination would be 1 %. However, if only 20 species were included, the power to discriminate would be 5 %. Therefore, to more accurately determine the proportion of species affected, the plotting position should be weighted for the number of species in the aquatic ecosystem which the surrogate species in the SSD are meant to represent. The proportion of species in the cumulative probability distribution was thus weighted (WSSD). In addition, different methods of manipulating weights of the taxonomic groups would affect values of HC_5. The SSD method allocates the same weight to the three groups when calculating the cumulative probability. Depending on weighting used, probabilities determined based on equally weighted SSD and plotting positions calculated by use of Eq. 1, values of the HC_5 can vary. For example, if the most sensitive species were more than 5 % in the environment but the $1/(n+1)$ was less than 5 %, the HC_5 would be greater than it should be and would result in underprotection. Thus, Forbes and Calow (2002) thought that the weight of vertebrate, invertebrate, and algae should be 0.1, 0.26, and 0.64, respectively, because these are the proportions of these species in the environment. Then, a WSSD curve, which represents the cumulative frequency of the actual proportions of species and or classes of species in the environment, could be constructed and more accurate HC_5 calculated. However, would this weighting proposed by Forbes and Calow (2002) be correct for Tai Lake? The weight of each of the three groups should be representative of the proportions of the three categories in Tai Lake. Three ways of manipulating the weight are given (Fig. S2).

In this study, proportions of categories in Tai Lake were determined (Su 2011). Since the categories surveyed were not classified into vertebrate, invertebrate, and algae, they were aggregated into three categories and their proportion as well. Weightings were determined based on the classification of individual species present to determine the proportions in the three categories.

Because only phylum-level proportions were available, all of species in the analysis were first classified to genera, and then genera into families and families into orders, orders into classes, and finally classes into phyla so that proportions in the three categories could be determined. If not, the weight was equally distributed (Fig. S3).

Assuming the weight of an upper level is *W*, when allocating the proportion to the next level, the weight was calculated based on the ratio among the classifications of the next level, which is expressed as P_1:P_2:…:P_n. Weighting coefficients of the next level were then calculated (Eq. 2).

If the proportion of each classification is documented, the P_i will be that value. However, if the proportions of a level were not available, the P_i will be equal to $1/n$.

Table 1 Acute toxicity of copper (Cu) to freshwater organisms (μg/L)

Phyla	Genera	Species	No.[a]	SMV	GMV
Bacillariophyceae	*Melosira*	*Melosira granulata*	1	2,580.00	2,580.00
Chlorophyta	*Chlorella*	*Chlorella vulgaris*	4	136.29	136.29
Chlorophyta	*Capricornutum*	*Pseudokirchneriella subcapitata*	10	263.45	263.45
Chlorophyta	*Chlamydomonas*	*Chlamydomonas reinhardtii*	2	47.00	47.00
Mollusca	*Corbicula*	*Corbicula fluminea*	1	2,600.00	2,600.00
Annelida	*Tubifex*	*Tubifex tubifex*	1	160.00	160.00
Chordata	*Ctenopharyngodon*	*Ctenopharyngodon idella*	4	138.08	138.08
Chordata	*Cyprinus*	*Cyprinus carpio*	14	186.37	186.37
Chordata	*Poecilia*	*Poecilia reticulate*	10	1,116.51	1,116.51
Chordata	*Lepomis*	*Lepomis macrochirus*	29	1,251.02	1,251.02
Chordata	*Anguilla*	*Anguilla japonica*	3	377.40	377.40
Chordata	*Oncorhynchus*	*Oncorhynchus kisutch*	12	40.71	49.47
Chordata	*Oncorhynchus*	*Oncorhynchus mykiss*	118	60.11	49.47
Arthropoda	*Cyclops*	*Cyclops* sp.	4	2,550.20	2,550.20
Arthropoda	*Orconectes*	*Orconectes limosus*	1	600.00	600.00
Arthropoda	*Gammarus*	*Gammarus* sp.	3	135.35	135.35
Arthropoda	*Daphnia*	*Daphnia magna*	146	8.03	10.89
Arthropoda	*Daphnia*	*Daphnia hyalina*	1	5.00	10.89
Arthropoda	*Daphnia*	*Daphnia pulex*	9	32.16	10.89
Arthropoda	*Ceriodaphnia*	*Ceriodaphnia dubia*	56	14.69	70.67
Arthropoda	*Ceriodaphnia*	*Ceriodaphnia rigaudi*	2	340.00	70.67
Arthropoda	*Moina*	*Moina macrocopa*	2	6.63	6.58
Arthropoda	*Moina*	*Moina irrasa*	5	6.53	6.58
Arthropoda	*Diaphanosoma*	*Diaphanosoma brachyurum*	1	950.00	950.00

[a] Quantity of species data

Weighting coefficients are calculated level by level and finally to the species level. For example, when calculating the weighting coefficients of species with acute data, the weight of algae is 22.7 % in all three categories and their two phyla in the algae category.

$$w_i = \frac{P_i}{\sum_1^n P_i} W(i = 1, 2, \ldots, n) \qquad (2)$$

The two phyla are *Chlorophyta* and *Bacillariophyceae*, and the ratio of these phyla is 39.5:16.1 (Su 2011); then, weighting coefficients were calculated from the weight of the algae category by use of this ratio. The resulting weighting coefficients of these two phyla are 16.1 and 6.6 %, respectively. For the phylum *Chlorophyta*, there is only one class, *Chlorophyceae*, so the class *Chlorophyceae* received the whole weight of 16.1 % from its phylum. In the class *Chlorophyceae*, there were two orders, *Chaetophorales* and

Table 2 Chronic toxicity of copper (Cu) to freshwater organisms (μg/L)

Phyla	Genera	Species	No.[a]	SMV	GMV
Cyanobacteria	*Arthrospira*	*Spirulina* sp.	6	215.44	215.44
Cyanobacteria	*Microcystis*	*Microcystis aeruginosa*	2	1.00	1.00
Chlorophyta	*Scenedesmus*	*Scenedesmus quadricauda*	1	10.00	10.00
Chlorophyta	*Chlamydomonas*	*Chlamydomonas reinhardtii*	2	21.49	21.49
Chordata	*Carassius*	*Carassius auratus*	6	82.60	82.60
Chordata	*Oncorhynchus*	*Oncorhynchus mykiss*	94	26.38	26.38
Arthropoda	*Gammarus*	*Gammarus* sp.	5	15.61	15.61
Arthropoda	*Daphnia*	*Daphnia magna*	55	28.32	18.67
Arthropoda	*Daphnia*	*Daphnia pulex*	12	12.31	18.67
Arthropoda	*Ceriodaphnia*	*Ceriodaphnia dubia*	72	27.60	27.60

[a] Quantity of species data

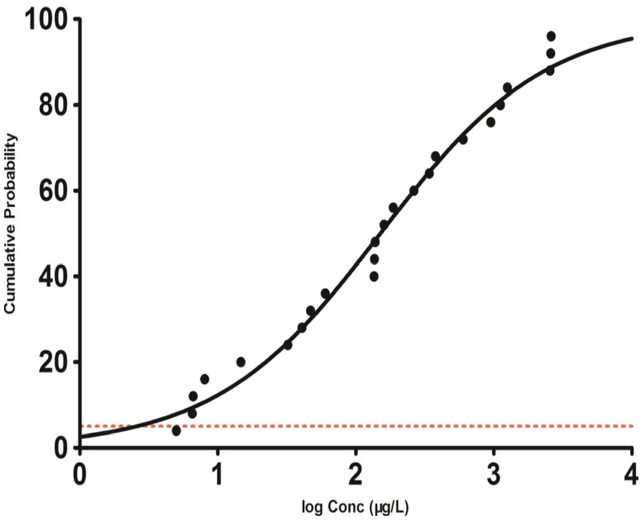

Fig 1 SSD acute toxicity of copper (Cu) based on all species. The *dashed line* represents the HC_5

Chlorococcales, and due to the lack of ratio between these two orders, they were assigned equal weights of 16.1 % from the class *Chlorophyceae*. Thus, weighting coefficients of these two orders are both 8.1 %. The same methods and process were applied to species levels. In this way, all species both in analysis of acute and chronic WQC were assigned weighting coefficients.

Construction of the WSSD

After obtaining the weight of each species for both acute and chronic criteria, the acute and chronic WSSD curves were constructed. The log of concentration for each LC_{50} or EC_{50} for acute and NOEC or LOEC for chronic were sorted from least to greatest then multiplied by their weighting coefficients and plotted as the WSSD, and the log-logistic model function was fitted to the data (Figs. 3 and 4 and Tables 3 and 4).

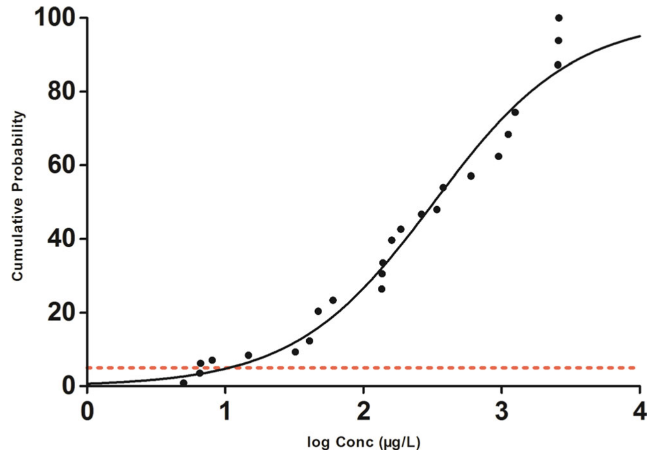

Fig. 3 Acute WSSD curve for all the species to copper (Cu). The *dashed line* represents the HC_5

Statistical analysis

The Kolmogorov-Smirnov and Shapiro-Wilk tests were both applied to determine whether the data could be described by a normal distribution for both raw and log-transformed data. The testing outcome ($p > 0.05$) indicated that all data were log-normally distributed. Figures were generated by use of GraphPad® Prism 5 software.

Selection of assessment factor and derivation of WQC

Due to uncertainties in calculating HC_5 values, application factors (AF), sometimes referred to as safety factors, varying from 1 to 5, were applied to the resulting HC_5 values to be conservative or more protective. The ratio of HC_5 and the AF value were used in combination to calculate the site-specific WQC. According to the Technical Guidance Document (TGD) (European Commission 2003), the following points were considered when selecting the AF: (1) overall quality of the toxicological database and the endpoints covered; (2)

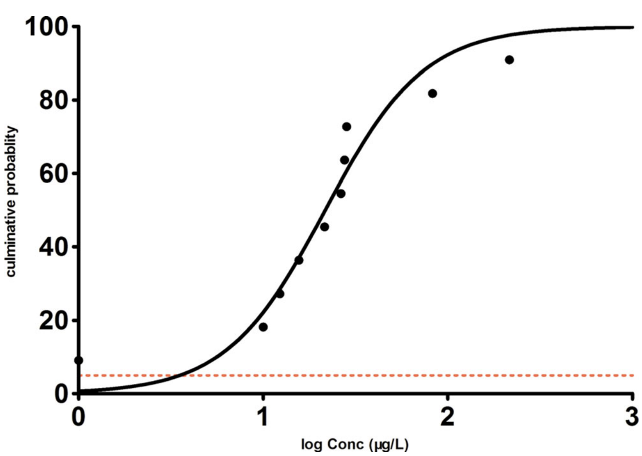

Fig 2 SSD for chronic toxicity of copper (Cu) based on all species. The *dashed line* represents the HC_5

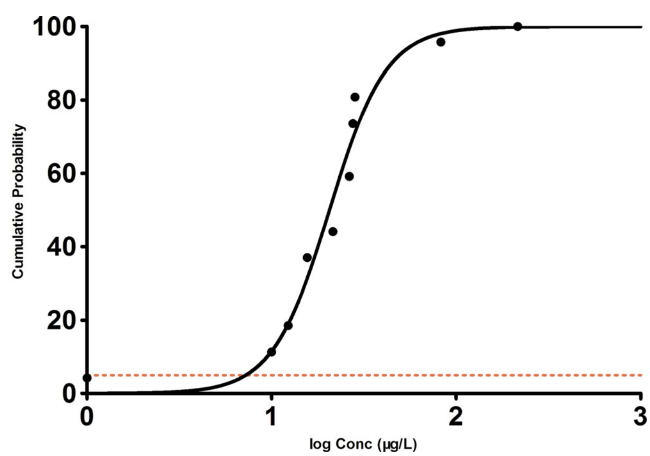

Fig. 4 Chronic WSSD curve for all the species to copper (Cu). The *dashed line* represents the HC_5

diversity and representativeness of the taxonomic groups covered by the database; (3) mode of chemical action, the statistical uncertainties around the fifth centile estimate; and (4) comparison between field/microcosm studies and the fifth centile. AF values are selected, and then the WQCs are calculated for both acute and chronic (Eqs. 3 and 4).

$$\text{Acute WQC} = \text{HC}_5(\text{acute})/\text{AF} \quad (3)$$

$$\text{Chronic WQC} = \text{HC}_5(\text{chronic})/\text{AF} \quad (4)$$

However, the AF can be altered and is determined by both the environmental and economic condition of a country. For example, in more developed countries, environmental protection agencies are inclined to develop more stringent and thus protective criteria so they assign larger AF values, like 2 in the USA, while in less developed countries, the AF is less. Earlier studies adopted an AF of 2 (Kooijman 1987; Van Sprang et al. 2004). In order to provide adequate protection for endemic species, in Tai Lake, the AF selected was 2.0.

Results and discussion

Variation within and among species

The issue of the variability within species and genera should be considered, as well as the variability observed among species and genera. Plots of variation for both acute and chronic species toxicity data are presented (Figs. 5 and 6). Plots of variation cannot be generated for all genera because for some genera, there was only one species.

Weightings for species

Weighting coefficients for algae, invertebrates, and vertebrates were collected (Su 2011) and aggregated (Fig. S1). For the algae category, the two phyla *Bacillariophyceae* and *Chlorophyta* had proportions of 6.6 and 16.1 %, respectively, of the 22.7 % of all species assigned to this category based on proportions in Tai Lake. The invertebrate category consisted of two sub-categories, zooplankton, and benthic fauna. The proportions of these groups were 28.9 and 18.5 %, respectively, of the total proportion of 47.3 % of species in the invertebrate category. Of the 28.9 % assigned to the zooplankton category, the phyla containing copepods and cladocera comprised 12.9 and 16.0 %. Other proportions have not been reported in the literature, so they were calculated as described above (Figs. S2 and S3). Acute and chronic data were weighted separately (Tables 3 and 4). Weighted and unweighted, cumulative probabilities are quite different. For example, when the concentration of Cu reaches 6.5 μg/L, 8.0 % of species would be affected, based on an unweighted cumulative probability, while if weighted, cumulative probabilities are used, and the proportion of species affected was 3.6 %. Weighting coefficients were calculated by using the proportion of species more representative of the proportion of a species in the environment than the $1/(n + 1)$. Thus, the HC_5 extrapolated from the WSSD method is a more rational concentration.

WQC value and differences in sensitivities among species

The acute HC_5 for copper was 10.6 while the chronic HC_5 was 7.3 μg Cu/L, respectively. Thus, based on AF of 2, the acute WQC was 5.3 and the chronic WQC was 3.7 μg Cu/L. By constructing the WSSD curve for both acute and chronic measures of toxic potency of species selected for Tai Lake, species from the families Daphnidae and Moinidae and phylum *Chlorophyta* were most sensitive to acute exposure to Cu. While species belonging to the phyla Chordata and Mollusca, like the bluegill sunfish (*Lepomis macrochirus*) and clam (*Corbicula fluminea*) were relatively insensitive to acute exposure to Cu. Species from the phyla *Cyanobacteria*, *Chlorophyta*, and Arthropoda were most sensitive, while those from the phyla Chordata and *Cyanobacteria* were more tolerant. Values for acute toxicity were greater than those for chronic exposures except for the family Daphnidae. This result is consistent with the fact that the water with copper contaminate is seldom acutely toxic to fishes that represented the phylum Chordata (McCormick et al. 1994). However, fishes are sensitive to chronic based on endpoints of growth, reproduction, and immune function (Baatrup 1999). Because Cu is acutely toxic to *Chlorophyta* but less toxic to fishes, Cu is widely used as an algaecide in aquaculture to kill filamentous algae (Chen and Lin 2001).

Comparison of WQC developed from WSSD and SSD

Two WQC based on the same acute and chronic toxicological data and AF values were derived by use of the SSD or WSSD methods (Figs. 1 and 2). The acute WQC values derived by use of the WSSD and SSD methods were 5.3 and 1.3 μg Cu/L, respectively. The unweighted SSD resulted in a lesser value which could have resulted in overprotection. The chronic WQC of 3.7 μg Cu/L predicted from the WSSD was also greater than the value of 1.8 μg Cu/L predicted by use of the unweighted SSD method. It is counterintuitive for an acute threshold to be less than a chronic threshold calculated by use of the SSD method. This was probably due to the lack of chronic toxicity data of some species that are more sensitive to Cu(II). Some less sensitive species contributed to a greater

Table 3 Weighted or unweighted cumulative probability for acute toxicity data

Species	SMV (μg/L)	Weighting coefficients (%)	Weighted cumulative probability (%)	Unweighted cumulative probability (%)
Daphnia hyalina	5.00	0.89	0.89	4.00
Moinairrasa	6.53	2.66	3.55	8.00
Moina macrocopa	6.63	2.66	6.21	12.00
Daphnia magna	8.03	0.89	7.10	16.00
Ceriodaphnia dubia	14.69	1.33	8.43	20.00
Daphnia pulex	32.16	0.89	9.32	24.00
Oncorhynchus kisutch	40.71	3.00	12.32	28.00
Chlamydomonas reinhardtii	47.00	8.07	20.39	32.00
Oncorhynchus mykiss	60.11	3.00	23.39	36.00
Gammarus sp.	135.35	3.08	26.47	40.00
Chlorella vulgaris	136.29	4.04	30.51	44.00
Ctenopharyngodon idella	138.08	3.00	33.51	48.00
Tubifex tubifex	160.00	6.16	39.67	52.00
Cyprinus carpio	186.37	3.00	42.67	56.00
Pseudokirchneriella subcapitata	263.45	4.04	46.71	60.00
Ceriodaphnia rigaudi	340.00	1.33	48.04	64.00
Anguilla japonica	377.40	5.99	54.03	68.00
Orconectes limosus	600.00	3.08	57.11	72.00
Diaphanosoma brachyurum	950.00	5.32	62.43	76.00
Poecilia reticulate	1,116.51	5.99	68.42	80.00
Lepomis macrochirus	1,251.02	5.99	74.41	84.00
Cyclops sp.	2,550.20	12.90	87.31	88.00
Melosira granulata	2,580.00	6.55	93.86	92.00
Corbicula fluminea	2,600.00	6.16	100.00	96.00

chronic threshold value, which was greater than the acute value, but the chronic threshold is less than the acute threshold calculated by the WSSD method. This result demonstrates that the WSSD method is more realistic and representative of the natural environment and allows more accurate, site-specific WQC. The cumulative probabilities of WSSD method are precise of the actual proportion of the ambient water in Tai Lake, so the HC_5 value is more likely to be the toxicity affecting 5 % of species in Tai Lake. Thus, the HC_5 calculated by the WSSD method is a better prediction value, so it should be widely spread in the WQC-related research, and more study on this method itself should be conducted.

Table 4 Weighted or unweighted cumulative probability for chronic toxicity data

Species	SMV (μg/L)	Weight coefficients (%)	Weighted cumulative probability (%)	Unweighted cumulative probability (%)
Microcystis aeruginosa	1.00	4.23	4.23	9.09
Scenedesmus quadricauda	10.00	7.12	11.35	18.18
Daphnia pulex	12.31	7.21	18.56	27.27
Gammarus sp.	15.61	18.48	37.04	36.36
Chlamydomonas reinhardtii	21.49	7.12	44.16	45.45
Oncorhynchus mykiss	26.38	14.99	59.15	54.55
Ceriodaphnia dubia	27.60	14.43	73.58	63.64
Daphnia magna	28.32	7.21	80.79	72.73
Carassius auratus	82.60	14.99	95.78	81.82
Spirulina sp.	215.44	4.23	100.00	90.91

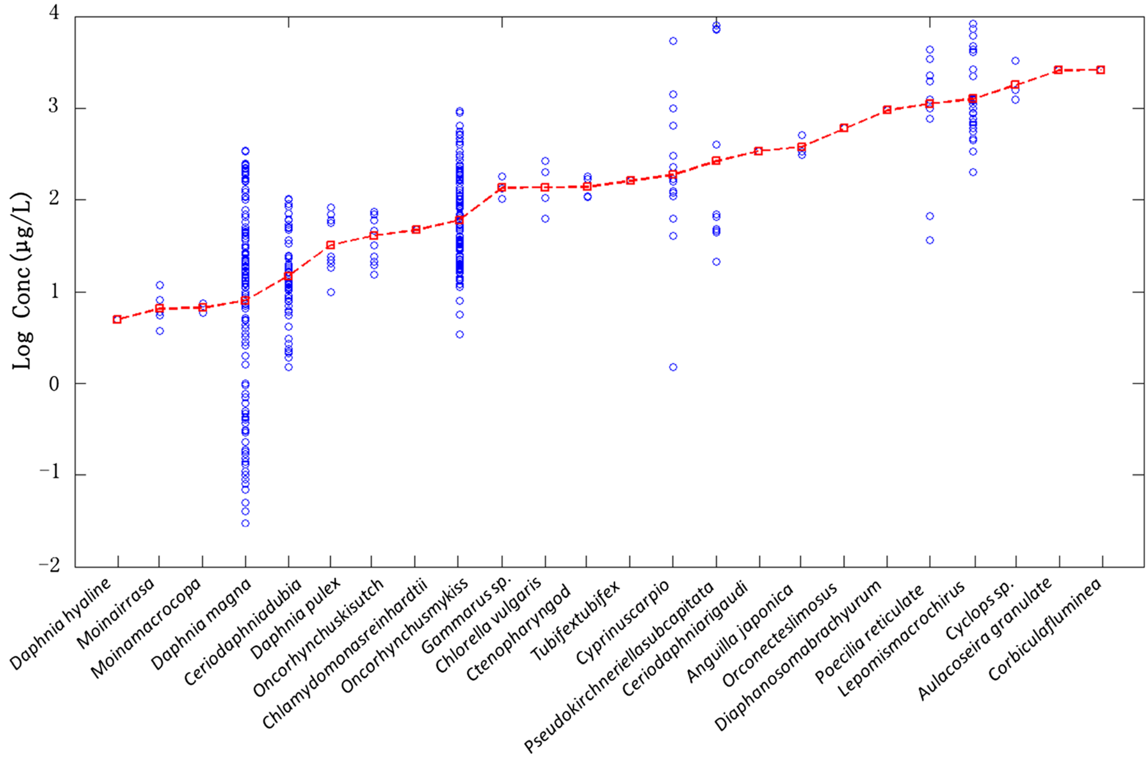

Fig. 5 Variation within and between different species with acute data

Comparison of WQC in different countries

The WQC derived for Cu was compared to those of the USA (US EPA 2006), Australia (ANZE 2000), and Canada (CCME 1999) and with the WQS of China surface water and waters used for fisheries (Table 5). Both the acute and chronic WQC derived for protection of the Tai Lake ecosystem by use of the WSSD method were less than the WQC for level I surface

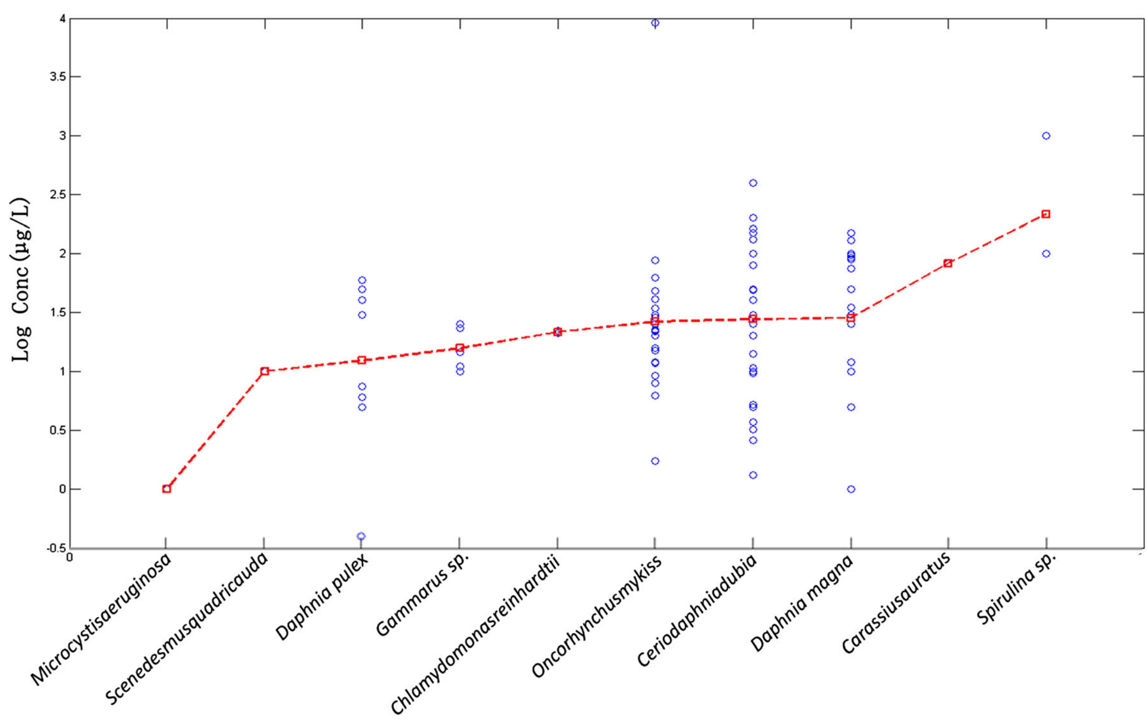

Fig. 6 Variation within and between different species with chronic data

water in China and the WQC of the USA derived from toxicity centile rank (TCR). Without calculating a site-specific WQC for the groups of species in Tai Lake, both the acute and chronic WQC developed by use of the unweighted SSD method were similar to WQC developed by Australia by use of the SSD fitted by use of the Burr III model, and the WQC of Canada derived by use of assessment factors but less than the WQS value for Chinese level I surface waters and the WQC value of the USA. The WQC for Cu derived for Tai Lake by use of the WSSD weighted for the proportions of species in Tai Lake was less than the WQC for Chinese level I surface water. While this indicates that the WQC might be underprotective of the effects of Cu, a final assessment would need to also consider the biologically available fraction by use of the biotic ligand model (BLM) (see below).

Differences between the WQC derived in our study and the WQC of other countries might be due to the different representative or dominant species selected. For example, Salmon fish were the dominant species in the Great Lakes of the USA, while cyprinoid fish were the primary kind of fish in Tai Lake. Also, the amount of phytoplankton is far more than other species in the Great Lakes, while in Tai Lake, the amount nearly equals that of other species. The kinds and relative proportions of the more sensitive species were different between China and the United States. In addition, different methods and models would also contribute to the differences of WQC in different countries.

When considering the appropriateness of site-specific WQC, bioavailability should be addressed. The toxicity data, like LC_{50} or EC_{50}, used to derive the WQC were from the database of ECOTOX, which were obtained from tests conducted under laboratory conditions. Under the natural conditions of surface waters, water chemistry such as pH, organic carbon content, hardness, and alkalinity, as well as other edaphic factors, will determine how much copper will be biologically available. Therefore, bioavailability should be taken into consideration. Based on the theory of BLM (Di Toro et al. 2001; Santore et al. 2001), only the copper ions binding to the biotic ligand are effective. For example, biotic ligand of fish appears to be sites on the surface membrane of the gill, thus effective copper ions are only those binding to this site. The binding process is influenced by water chemistry condition (Chapman et al. 1998) and competition with other metal ions binding to biotic ligand. The bioavailability can be demonstrated in the figure (Fig. S4). The bioavailability of copper is able to be predicted by the BLM (version 2.2.3), depending on the site-specific water condition. When a number of water chemistry indexes of Tai Lake, such as pH, hardness, and alkalinity, are available, the BLM (version 2.2.3) can be used to calibrate the toxicity of Cu^{2+}.

There has been much discussion of whether SSDs should be weighted and which of the various models should be used to fit functions to the data (Mu et al. 2014; Wu et al. 2013). In general the differences among these different approaches are less than a factor of 10, which is fairly small when the uncertainties are associated with bioavailable fraction and keystone species that might or might not be identified. Furthermore, the uncertainties are associated with protection of ecosystem structure and function from chronic effect of small concentrations of mixtures of contaminants. Finally there is the issue of protection of organisms at the top of the food chain, including wildlife that might not live in the water but eat aquatic organisms. To protect these "aquatic" species, it requires consideration of persistence and potential for bioaccumulation, bioconcentration, and biomagnification (Su et al. 2014; Zhang et al. 2013; 2014).

Future research

The choice of toxicological endpoints affects WQC that are developed. The measurement endpoints are usually mortality, inhibition of growth, and maximal no-effect concentration in most assessments. In this study, the LC_{50} or EC_{50} was chosen as the acute endpoints, and NOEC or LOEC was treated as the chronic endpoints which have been commonly used in most WQC derivation with the SSD method. In future developments of WQC, refinements of endpoints might result in better protection such as biomarkers, physiological, and molecular markers with the improvement of toxicological tools (Chen et al. 2014; Li et al. 2013; Yin et al. 2003).

Table 5 Comparison between freshwater aquatic criteria and standards for copper (Cu) (μg/L)

WQC source	Derivation methods	WQC in fresh water		WQS of surface water (China)					WQC of fishing water (China)
		Acute threshold	Chronic threshold	I	II	III	IV	V	
This study	SSD/WSSD	1.3/5.3	1.8/3.7	10	1,000	1,000	1,000	1,000	10
USA	TCR	13	9						
Australia	SSD	1.4							
Canada	AF	2~4							

SSD species sensitivity distribution, *WSSD* weighted species sensitivity distribution, *TCR* toxicity centile rank, *AF* assessment factors

Conclusion

The WQC derived by use of the WSSD method, which was based on endemic species in Tai Lake, was different from that derived by use of unweighted SSD method. Alternatively, the surface water standard now used in Chinese environmental management is greater than the site-specific WQC derived for Tai Lake. Therefore, a risk of "underprotection" for exposure of specific species in Tai Lake to Cu might exist. However, future work on speciation of Cu and its bioavailability in Tai Lake should also be considered when determining whether the current WQC is sufficient to protect the range of endemic species.

Acknowledgments This work was jointly funded by the National Natural Science Foundation of China (No. 21377053 and 20977047), Major National Science and Technology Projects (No. 2012ZX07506-001 and 2012ZX07501-003-02). Prof. Giesy was supported by the program of 2012 "High Level Foreign Experts" (No. GDW20123200120) funded by the State Administration of Foreign Experts Affairs, the People's Republic of China to Nanjing University, and the Einstein Professor Program of the Chinese Academy of Sciences. He was also supported by the Canada Research Chair program, a Visiting Distinguished Professorship in the Department of Biology and Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong. Great thanks to David Saunders, a vanier scholar in ecotoxicology studying in Toxicology Centre, University of Saskatchewan, for his time in polishing our manuscript.

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