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An often-overestimated ecological risk of copper in Chinese surface water: bioavailable fraction determined by multiple linear regression of water quality parameters

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Abstract

Background Risks of adverse ecological effects of copper (Cu) consider of water quality parameters were not fully understood in China. Here, a national-scale exposure of Cu in Chinese surface water was investigated, and the first report using multiple linear regression approach to predict and correct toxicity data based on water chemistries in China. Risk of Cu was overestimated without considering water quality parameters in the previous studies.

Results Under prevalent water quality conditions of hardness = 150.0 mg/L, pH = 7.8, and dissolved organic carbon (DOC) = 3.0 mg/L, across China, the predicted no effect concentration for total, dissolved Cu was 9.71 μg/L. Based on results of the preliminary risk quotients method, 1.19% (a total of 43 in 3610 sites) were classified as "high risk", only one sixth of the percentage of sites with "high risk" than the proportion predicted when not considering water quality parameters, which was 7.51%. Similar results were obtained by application of both the margin of safety method (0.71% compared to 2.81%) and joint probability curve method (3.34% compared to 16.29%), both of which overestimated risks posed by Cu to aquatic organisms in China.

Conclusion After correcting for bioavailability based on water quality parameters, consider both concentrations and frequencies during ecological risk assessment, regions of China at greatest risk from adverse effects of Cu were the Hai River (*Haihe*), Huai Rivers (*Huaihe*) and Chao Lake. These findings provide a comprehensive method for a more accurate assessment of risks of adverse effects of Cu to aquatic life in surface waters.

Keywords Metal bioavailability, Ecological risk assessment, Simulation models, Water quality, Available fraction, Chemical activity

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Background

Aquatic organisms in surface freshwater can be exposed to a variety of chemicals discharged during activities of humans. Various chemical substances, including inorganic compounds like metals and metalloids and organic chemicals are widely distributed and frequently occur at elevated concentrations in aquatic environments, which can result in various adverse effects [1–4]. Concentrations of the transition metal copper (Cu) present in surface freshwater pose greater risks to aquatic species than other priority metal/metalloid pollutants, such as chromium (Cr), cadmium (Cd), lead (Pb), mercury (Hg) and arsenic (As) and some focus of attention organic pollutants, such as nonylphenol, ethinylestradiol, linear alkylbenzene sulfonate and pharmaceuticals and personal care products that have been reported for various regions China, the United Kingdom, Japan and other countries [3, 5–7]. Approximately 99.9% of aquatic organisms were predicted to be affected by Cu in surface water of Tai Lake, China [8, 9]. Proportions of samples from the coastal marine environment of China, which exceed hazard quotients (HQs) of 1.0, decreased from 64% in 2005 to 31% in 2012, but potential ecological risks of Cu remained relatively great, especially in Liaodong and Bohai Bays, and the Yellow River Estuary [10]. As a highly ranked relative risk chemical, more than 600 publications concerning toxicity of Cu to aquatic organisms have been published over the last five years [4]. On a national-scale few ecological risk assessments considering total concentrations of Cu and have seldom considered effects of water quality parameters on toxicity of Cu in Chinese surface water, and this study would reference for water quality standard revised in China.

Toxicity of Cu to aquatic organisms is dependent on various accessory, physicochemical characteristics of surface water, especially chemical speciation related to water quality parameters, such as pH, hardness and dissolved organic carbon (DOC) [11–15]. Hardness-dependent corrections of toxic potency of Cu was the earliest and most widely used criterion in water quality criteria studies regarding metals [14]. Eco-toxicity data for Cu were normalized by hardness-based equation accord with procedures for development of site-specific water quality criteria (WQC) in the United States of America (USA) [14, 15]. Early ambient water quality criteria for Cu, developed in the USA, considered bioavailability by the use of an exponential equation to describe the relationship of Cu toxicity to hardness by performing a least squares regression of the natural logarithms of the acute values [ln(LC_{50})] on the natural logarithms of hardness [ln(hardness)]. When this was done the regression slopes of ln(LC_{50}) vs. ln(hardness) for Cu was determined to be 0.94 [14]. Later work showed the regression slopes of ln(LC_{50}) vs ln(hardness) for divalent transition metals, including Cu were approximately 1.0 [16]. It has long been recognized that dissolved organic matter in surface waters can interact with metals. Naturally occurring ligands of humic and fulvic acids can form stable complexes with metals and subsequently reduce their bioavailable fractions. This is particularly true for divalent, transition metals such as Cu [17–20].

As the analytical chemistry and computational power of computer improved, the quantitative understanding of the relationships between toxicity of metals and water quality parameters, such as pH value, hardness and DOC, that controlled speciation of metals have been described [25]. A semi-mechanistic model, based on hydro chemical equilibrium called the biotic ligand model (BLM) was developed, and its ability to predict toxicity of metals like Cu to aquatic organisms has been verified [21, 26, 27]. However, the BLM requires multiple input variables and is complex, and few states or governments adopted BLM-based Cu criteria or water quality standards. Site-specific criteria have been developed by use of the same basic methodology used by the USEPA to derive hardness-based criteria, but also included DOC and pH [28]. As an initial proof of concept, a stepwise multiple linear regression (MLR) model for species that have been developed and tested over a range of DOC, pH and hardness conditions. The MLR and BLM models predicted species-specific toxicity with similar accuracies. A stepwise MLR for species, which has been tested over ranges of DOC, pH, calcium (Ca^{2+}) and magnesium (Mg^{2+}) or (taken together) have been developed to predict bioavailability [22, 27] and toxicity of nickel (Ni) [24, 25] and aluminum (Al) [31, 32] as well as Cu [32, 33]. The MLR model to predict toxicity of Cu is comparable to the BLM [34]. However, applications of MLR models to predict bioavailability of metals have been focused on North America, Oceania and Europe for the development of protective values for aquatic life [27, 29, 30, 32, 34].

The goal of ecological risk assessment is to protect specific environments and provide a theoretical basis for management releases of environmental risks posed by releases of materials during activities of humans. It provides a theoretical basis for the standard and criteria of pollutants for environmental management. Ecological risk assessments are used by risk managers in achieving protection environmental goals established by laws and regulations [35, 36]. Risk assessments are applied with regulations to derive an environmental quality standard (EQS) based on an appropriate predicted no effect concentrations (PNEC). Historically, without considering water quality parameters, risks posed by Cu to aquatic organisms have been overestimated because of inorganic and organic ligands represented by hardness and DOC, respectively, in surface water [37, 38]. Therefore, it was decided to apply MLR models, as well as hardness-based models and BLM to predict bioavailability of metals and in particular to develop a stepwise MLR model of to predict site-specific toxicities of Cu for use in assessments of risks to surface waters of China and compared to hardness-based models and BLM. In this study, the MLR model was applied to predict Cu toxicity under different water quality parameters. MLR models of Cu in surface waters of China were then used to address ecological risk assessment considering the metal bioavailability in surface freshwater. A hazard quotients method, margin of safety method and joint probability curves distribution were then applied to assess the potential ecological risks of Cu in surface water in seven major river basins, three major areas and five lakes of China.

Materials and methods

Data collection

Concentrations of Cu were collected and collated for China from data on Chinese rivers and lakes, collected by the China National Environmental Monitoring Centre (CNEMC). Distributions of concentrations of Cu in surface waters were tested for normality then categorized into seven major river basins, three major areas and five lakes. In detail, fifteen regions were made up of the Yangtze River (YZR), Yellow River (YR), Pearl River (PR), Songhua River (SHR), Huaihe river (HHR), Haihe River (HaiHR), Liaohe River (LHR), Zhemin area (ZMR), Xibei area (XBR) and Xinan area (XNR), five major lakes named Tai Lake (THL), Dianchi lake (DCL), Chao lake (CHL), Poyang lake (PYL) and Dongting lake (DTL).

Values for water quality parameters (such as pH value, hardness and DOC) required for development of the MLR models were assembled independently. Information on pH was assembled from monitoring data for Chinese rivers and lakes collected by the CNEMC. Information on hardness and DOC was obtained from recent publications and government reports published between 2001 and 2020 by performing searches in the China Knowledge Resource Integrated Database (CNKI) and Web of Science.

Data for acute toxicity of Cu to aquatic organisms (such as *Ceriodaphnia dubia, Daphnia magna, Pimephales promelas and so on*) were based on the water quality criteria (WQC) documents for Cu published by the U.S. Environmental Protection Agency (USEPA) and subsequently updated works [15, 28]. Toxicity data for China were assembled using the recent publications collected from CNKI and Web of Science. The toxicity of Cu to aquatic organisms including invertebrates and fish except plants. Evaluation criteria used to screen data on toxic potency of Cu to aquatic organisms were: (1) toxicity tests were conducted by use of standard methods [39]; (2) measured concentrations rather than nominal values were provided; and (3) accessory water quality parameters, including hardness (HD), alkalinity, pH and DOC were provided as well as concentrations of the following ion, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, SO_4^{2-}, Cl^{-} and temperature.

Toxicity data analysis

Distributions of concentrations of Cu were tested for normality, and all raw data and normalization data met the assumption of being normally distributed (Kolmogorov–Smirnov > 0.05). The hazardous concentration for 5% species affected (HC_5) value of Cu was calculated by use of the species sensitivity distribution (SSD) method as described previous previously [44, 45]. Briefly, the correlation of the concentration value and the cumulative probability fitted to non-linear curves with various models to derive the HC_5 of toxicity, which represents the 0.05 cumulative probability of toxicity data.

The toxicity data were normalized based on the MLR model and compared with hardness-based model and BLM that have been used by US EPA in the report of "aquatic life ambient freshwater quality criteria – Copper".

(1) Multiple linear regression model

MLR models for Cu were developed following previously described methods [28, 33]. Three toxicity modifying factors (TMFs), hardness, pH and DOC, were considered. Species-specific MLR models with TMF interactions were first developed by use of a stepwise linear regression approach. Toxicity data for the same species spanned a minimum range of 100 mg/L and the greatest hardness was at least three times that of the least. Toxicity tests spanned a minimum range of other water chemistries including: 2.5 mg/L for DOC, and 1.5 pH units. Finally, nine species-specific MLR models (5 invertebrates and 4 fish) have been available for development of the pooled acute MLR model in this research and have been added three species-specific MLR models compared with Brix et al. in [34]. After this initial evaluation, a pooled model was developed by use of previously described methods [28]. In brief, the basic form of a species-specific equation was developed (Eq. 1).

$$\ln(\text{Toxicity}_i) = \text{Intercept}_i + k_{1i} \times \ln(\text{HD}) + k_{2i} \times \text{pH} + k_{3i} \times \ln(\text{DOC}) + \text{error}_i \quad (1)$$

where hardness (HD) and DOC are expressed as mg/L; toxicity of Cu is expressed in μg/L; coefficient k_{ai} is defined the selected species; and intercept_i is the species-specific intercepts. For the pooled model, coefficient k_{ai}

is defined for all the toxicity data in the species-specific models.

Acute toxicity value was standardized to a target water condition, using the species-specific MLR models or pooled MLR model when lacked species-specific MLR model (Eq. 2).

$$\begin{aligned}&\text{Standardized LC}_{50}\\&=\exp[\ln(\text{LC}_{50\text{meas}})-\text{HD}_{\text{slope}}(\ln\frac{\text{HD}_{\text{meas}}}{\text{HD}_{\text{target}}})\\&\quad-\text{pH}_{\text{slope}}(\text{pH}_{\text{meas}}-\text{pH}_{\text{target}})\\&\quad-\text{DOC}_{\text{slope}}(\ln\frac{\text{DOC}_{\text{meas}}}{\text{DOC}_{\text{target}}})]\end{aligned} \quad (2)$$

where LC_{50meas} = Observed LC_{50}; HD_{slope}, pH and DOC_{slope} form the pooled model; HD_{meas} is the tested water hardness; HD_{target} is the targeted hardness; DOC_{meas} is the tested water DOC concentration; DOC_{target} is the targeted DOC; pH_{meas} is the tested water pH; and pH_{target} is the targeted pH.

(2) Hardness-based model

The toxicity data for Cu were normalized by the hardness-based equation according to procedures outlined in the USA WQC reports [14, 15]. Detailed information for development of hardness-based equations can be found in the Additional file 1: Table S5.

(3) Biotic ligand model

The biotic ligand model (BLM version 2.2.3) is fundamentally an equilibrium-based speciation model, which has gained widespread interest among some more developed countries and regions.

Ecological risk assessment method

To provide a more rigorous scientific basis and technical support for risk management options for Cu, three ecological risk assessment methods including screening-level and high-level assessment were applied and compared in this study, respectively (Fig. 1).

Risk quotients, overall preliminary risk assessment

First, risk quotients (RQs) were used as risk indices (Eq. 3).

$$\text{RQ}_s=\frac{\text{EC}_s}{\text{PNEC}} \quad (3)$$

where ECs is the environmental concentrations of Cu in surface water, and PNEC is the predicted no-effect concentration of Cu to aquatic organisms.

Acute toxicity data and an assessment factor (AF) were used to determine the PNEC (Eq. 4).

$$\text{PNEC}=\frac{\text{HC}_5}{\text{AF}} \quad (4)$$

where HC_5 is the 5th centile concentration of the species sensitivity distribution (SSD) for as an effect index of Cu to aquatic organism, it was used as an effect index of Cu, and the AF was used to take 3.22 (freshwater final acute-chronic ratio) in this study [15].

The risk assessment of Cu was classified as insignificant: When the values of $RQ \geq 1$, a large risk is expected; the values of $0.1 \leq RQ < 1$ indicate moderate risk and the values of $0.01 \leq RQ < 0.1$ indicate minimum risk.

Prioritization indexes (*PI*) based on considering frequency of PNEC exceedance in different regions.

There is a tendency to consider both concentrations and frequency during ecological risk assessment. *PI* was calculated (Eq. 5).

$$\text{PI}=\text{RQ}\times\text{F} \quad (5)$$

where PI is the prioritization index; RQ is the risk quotient calculated based on the 50th percentile concentration and PNEC; and F is the frequency of concentrations exceeding PNEC. F indicates the share of sites where potential effects are anticipated (Eq. 6) [40].

$$\text{F}=n/\text{N}\times 100\% \quad (6)$$

where n is the number of sites with concentrations above PNEC, and N is the total number of sites.

Probabilistic ecological risk assessment, a refined risk assessment considering various water quality parameters.

Use of risk quotients (RQ) is a preliminary risk assessment approaches, thus we also used a more probabilistic method for further assessment of potential effects of Cu on aquatic organisms. Probabilistic methods constitute one of several approaches that may be used for higher-tier assessments, which can better protect the complex ecosystems [7, 39]. A margin of safety (MOS) can quantify the extent of overlap between the distributions of environmental exposure concentrations and toxicity data. The MOS_{10} values were calculated (Eq. 7).

$$\text{MOS}_{10}=\frac{\text{C}_{0.1}}{\text{C}_{0.9}} \quad (7)$$

where $C_{0.1}$ is the 10th centile value for the toxicity data distribution and $C_{0.9}$ is the 90th centile value for the environmental exposure concentration (ECD) distribution.

Based on constructed toxicity SSD and environmental ECD curves, the MOS_{10} were obtained by comparing $C_{0.1}$ toxicity (SSD curve at 10% concentration) and $C_{0.9}$ exposure (ECD curve at 90% concentration) [41]. The range

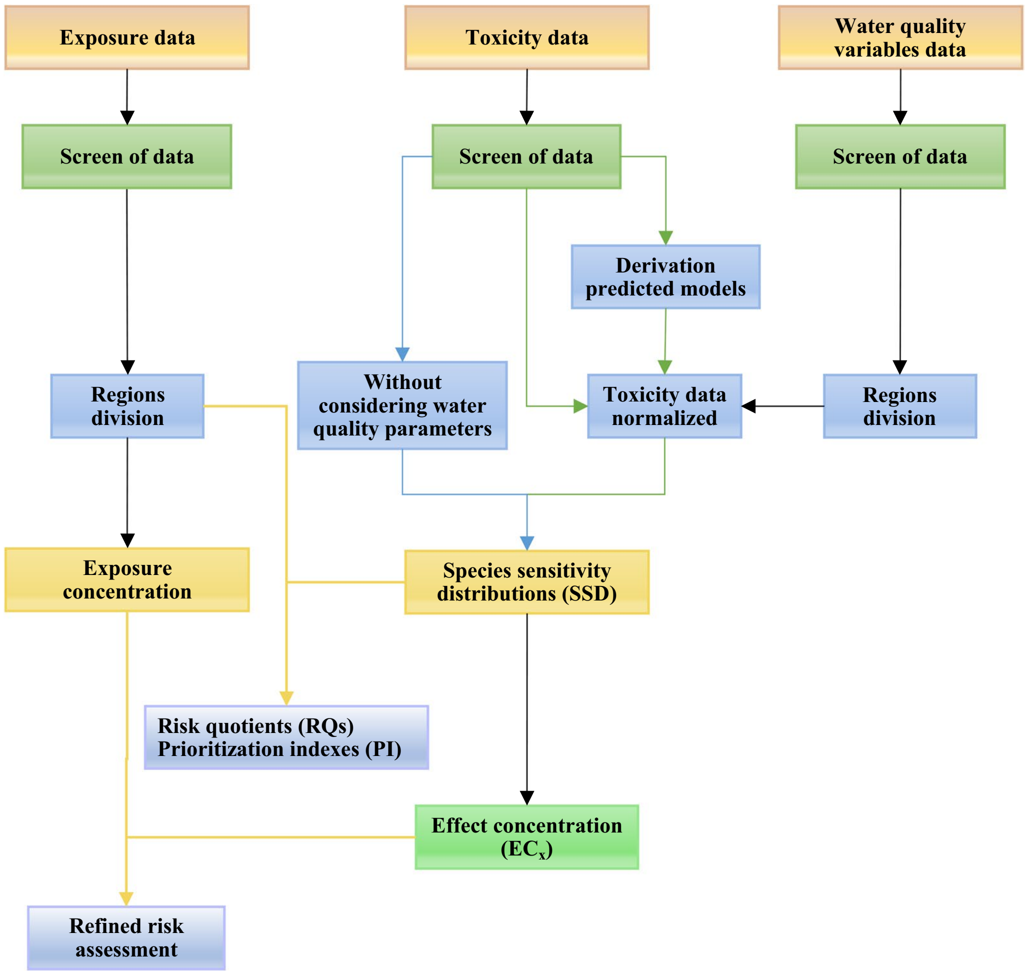

Fig. 1 Procedure for assessment of ecological risk for copper (Cu) applied in the present study

$0 < MOS_{10} < 1$ suggests potential risks, whereas $MOS_{10} \geq 1$ suggests de minimis risks to aquatic communities.

The joint probability distribution was used to describe the risk of Cu to aquatic organisms in this study following the method of previously works in our group [7, 9, 39, 42]. In addition, confidence limits were calculated to determine the probability that 10% of species would be affected with a 95% confidence interval around that estimate.

Data analysis

Origin 2019 (OriginLab Corporation, Northampton, Massachusetts, USA) was used to construct ECD and SSD curves for Cu. The statistical package SPSS for Windows 22.0 (SPSS Inc., Chicago, Illinois, USA) was used for statistical analyses. Kolomogorov–Smirnov tests did not show significance ($p < 0.05$). Since there was no strong reason to reject normality, the data were assumed to be sufficiently described by the normal probability distribution.

Results and discussion

Concentrations of Cu

In China, there are 3,610 sites for which concentrations of total dissolved Cu were collected by CNEMC in 2021 (Fig. 2a). Concentrations of Cu were normally distributed (Kolmogorov–Smirnov > 0.05). The mean concentration of total dissolved Cu was 1.97 μg Cu/L, with concentrations ranging from 0.04 to 179.0 μg Cu/L. Among the 15 regions, mean concentrations of total dissolved Cu in seven regions were greater than the overall mean in the following order: 3.16 μg/L (XNR), 2.67 μg/L (CHL), 2.58 (XBR), 2.48 μg/L (YR), 2.25 μg/L (HHR), 2.10 μg/L (PR), 1.99 (THL). The location with greatest concentration of Cu in surface water was in the XBR region (179 μg/L), followed by a location in the XNR region (137 μg/L) (Detailed information Table S1).

Concentrations of Cu in this study were consistent with those reported previously where the mean in water were 2.44 with a range of less than the limit of detection to 343 μg Cu/L in the Yangtze River (1314 sites), but less

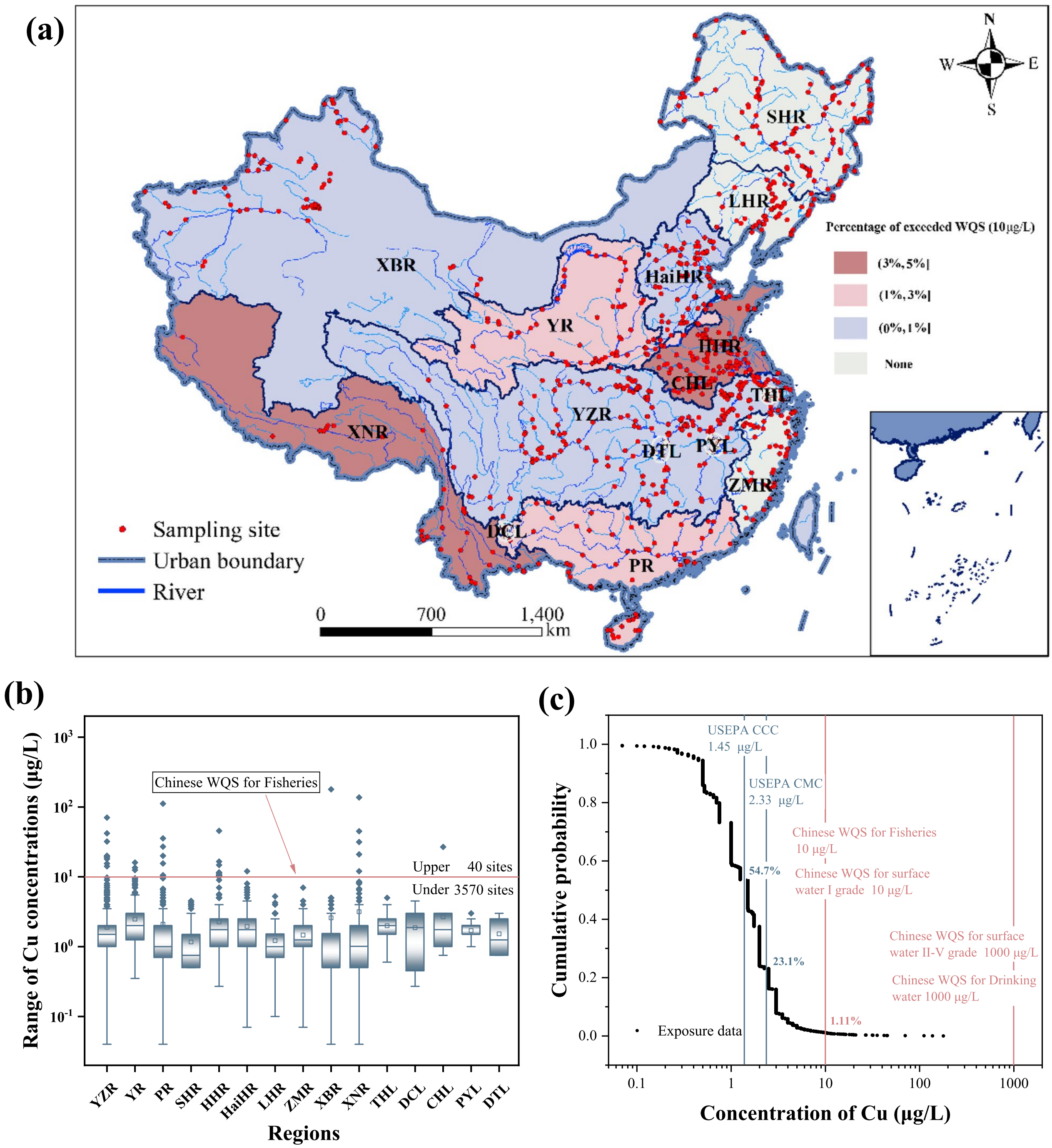

Fig. 2 Concentrations of total dissolved Cu in surface water in the 15 regions: Sampling sites and percentage of exceeded the water quality standard (WQS; 10 μg Cu/L) in 15 regions (**a**); sites numbers of exceeded the WQS in the 15 regions (**b**); Cumulative probability of concentrations of Cu in Chinese surface water and compared with Chinese WQS, along with the USEPA criteria (**c**)

than concentrations reported by other researchers which were 19 (2.40–171) μg Cu/L in Tai Lake (40 sites) [7, 40]. In other areas, mean concentrations of Cu in water were 1.66 (0.10–5, 320) μg Cu/L in the United Kingdom (UK) (89, 604 sites) [40]. Mean concentrations of Cu in five rivers of Tokyo, Japan was 4.0–10.0 μg Cu/L [4]. Mean concentrations of Cu in this study in China were between those reported for the UK and Japan.

The water quality standard (WQS) for Cu surface water in China is 10 μg Cu/L classified as grade I, but 1,000 μg

Cu/L in grades II to V. Cu is more toxic to aquatic organisms than to humans [43]. WQS for the protection of fisheries in Chinese waters from adverse effects of Cu is 10 μg Cu/L. In surface waters of China concentrations of Cu exceeded the WQS for protection of fisheries at 40 of 3610 sites (1.11%) (Fig. 2b), which is less than those reported for 2016, when concentrations of Cu in 45% of samples of water from Tai Lake exceeded WQS for the protection of fisheries [8].

In 2007, the USEPA revised aquatic life ambient freshwater quality criteria for Cu [15], the criterion maximum concentration (CMC) was set at 2.33 μg Cu/L, and a criterion continuous concentration (CCC) was set at 1.45 μg Cu/L under the water quality parameters which were 85 mg/L for hardness, 7.5 for pH and 0.5 mg/L for DOC. Concentrations of Cu in surface waters at 23.10% of sites (834 out of 3610 sites) in China exceeded the CMC, and 54.72% (1935 out of 3610 sites) exceeded the CCC without considering water quality parameters (Fig. 2c). Toxicity of Cu in water to aquatic organisms is dependent on chemical speciation related to the water quality parameters. Results of previous research have shown an inverse relationship between toxicity of Cu and inorganic and organic ligands, represented by hardness and DOC, respectively. So, it was not surprising that concentrations of Cu in Chinese surface water posed greater risk to aquatic organisms in waters where hardness and DOC were less.

Water quality variables

The necessary information was available to calculate TMFs of surface water including for each of the 15 regions of China. A total of 480 hardness data were collected from 40 publications, along with 897 DOC concentrations data from 50 publications, and 3578 pH data were collected from CNEMC. According to our survey, hardness of surface water in China ranged from 12.08 to 1007 mg/L, the arithmetic and geometric mean hardness were 146.8 and 125.8 mg/L, respectively. The 5th, 10th, 20th and 50th centiles of hardness were 37.29, 44.38, 80.96 and 152.7 mg/L, respectively. Values of pH ranged from 6.24 to 9.98, with an arithmetic mean of 7.77, with 5th, 10th, 20th and 50th centiles of 6.90, 7.09, 7.29 and 7.76, respectively. Concentrations of DOC ranged from 0.5 to 45.2 mg/L, with arithmetic and geometric means of 4.3 and 3.0 mg DOC/L. The 5th, 10th, 20th and 50th centiles for concentrations of DOC were 0.9, 1.2, 1.5 and 3.0 mg/L, respectively (Additional file 1: Table S2). As shown in Additional file 1: Table S3: The 50th centiles of hardness, pH and DOC were 152.7 mg/L, 7.8 and 3.0 mg/L, respectively. There were 136 samples for which concentrations of Cu and water chemistry from the same water body, the median values of hardness, pH and DOC in those samples were 162.3 mg/L, 7.9 and 3.0 mg/L, respectively. Therefore, the standard of normalized water quality parameters in China for MLR model in this study were 150.0 mg/L (for hardness), 7.80 (for pH) and 3.0 mg/L (for DOC), and the hardness-based model was 150 mg/L for hardness in China. A total of 136 samples for which all the water quality parameters required for developing the BLM model in China, were available and from these suggested, standard of normalized input variables for BLM were derived, which were 150.0 mg/L (for hardness), 7.80 (for pH), 3.0 mg/L (for DOC), 45 mg/L (for Ca^{2+}), 9 mg/L (for Mg^{2+}), 13 mg/L (for Na^{+}), 2.6 mg/L (for K^{+}), 55 mg/L (for $SO_4{}^{2-}$), 20 mg/L (for Cl^{-}), 95 mg/L (for Alkalinity) and 0.3 mg/L (for S^{2-}). The standard of normalized water quality parameters selected for use in China were significantly different from those suggested by the US EPA for use in the USA, which were 85 mg/L for hardness, 7.5 for pH and 0.5 mg/L for DOC (Additional file 1: Table S3) [15]. Median and mean of hardness and DOC content in surface water in China are generally greater than those in the USA.

Normalization of toxicity data

Data on acute toxicity of Cu used for normalization model development are shown in (Table S9). Values for acute lethality for Cu as well as hardness and DOC were natural log transformed. The log-transformed toxicity and TMFs [ln(hardness), ln(DOC), pH, etc.] tended to be linear and the slopes of the ln(toxicity) vs. ln(TMFs) varied among species. There were nine species that had sufficient toxicity data to develop species-specific acute toxicity MLR models, and a pooled MLR model was developed in Additional file 1: Table S4. The HD, pH and DOC slopes forming the pooled model were used to standardize the acute toxicity value without species-specific models in the acute SSD to the target water chemistry of interest. The resulting standard of normalized acute MLR model was expressed (Eq. 8).

$$\begin{aligned}\text{Standardized } LC_{50} &= \exp[\ln(LC_{50}) - 0.555(\ln\frac{HD_{meas}}{150}) \\ &\quad - 0.487(pH_{meas} - 7.8) - 0.29(\ln\frac{DOC_{meas}}{3.0})]\end{aligned} \tag{8}$$

where HD_{meas} is the test water hardness (5.0–1, 000 mg/L); DOC_{meas} is the test water DOC concentration (0.05–32.9 mg/L); and pH_{meas} is the test water pH (5.5–9.0).

The hardness-based model and BLM were also used to normalized toxicity data based on the standard water conditions and compared with the MLR model. The results are shown in Additional file 1: Fig. S1. The resulting normalized acute hardness-based model is expressed (Eq. 9) (Additional file 1: Table S5).

$$\text{Standardized } LC_{50} = \exp[\ln(LC_{50}) - 0.962(\ln\frac{HD_{meas}}{150})] \quad (9)$$

In total, 46 species were normalized by the MLR model and hardness-based model, and 45 species were normalized by use of the BLM model based on toxicity data (Additional file 1: Table S6).

Assessment of ecological risks posed by Cu

Risk quotients (RQs)

The correlation of the concentration value and the cumulative probability were fitted to various non-linear models to derive the HC_5 of toxicity, and the logistic model best fitted the data (Additional file 1: Fig S2). The acute HC_5 values of Cu under the standard water quality parameters based on the MLR model, BLM model and hardness-based model to aquatic organism were 31.27, 27.29 and 42.68 μg/L, respectively. The acute HC_5 value of Cu to aquatic organism was 10.69 μg/L based on raw toxicity data without considering water quality parameters. The PNEC of Cu was 9.71, 8.47 and 13.25 μg/L based on the MLR model, BLM model and hardness-based model under standard water quality parameters, while the PNEC of Cu was 3.32 μg/L under the raw toxicity data without normalization of water quality parameters (Fig. 3a). The acute HC_5 values based on the standardized of toxicity data among different models were different. Under the standard water quality parameters, the PNEC of Cu calculated based on BLM and MLR models were close, while the hardness-based model was slightly higher. However, the PNEC value is significantly lower without considering water quality parameter, because the raw toxicity data always used low hardness and DOC data for toxicity experiments, especially some experimental water was artificially added with low hardness and DOC, resulting in an increase in copper bioavailability and increased biological sensitivity.

Compared with several existing values for Cu criteria in China, it was reported that the median toxicity data of Cu was 70 μg Cu/L, and the concentration that would be hazardous for at least 10% of the tested species was 10 μg Cu/L [40]. The short-term HC_5($STHC_5$) calculated by use of the SSD method was 30.0 μg uuC/L and the long-term HC_5 ($LTHC_5$) was 9.44 μg Cu/L [46]. Using the same method, the $STHC_5$ and $LTHC_5$ were calculated to be 30.9 and 4.10 μg Cu/L [47]. A BLM-based WQC for Cu in Tai Lake, and the CMC and CCC were calculated to be 32.19 and 9.70 μg Cu/L under specific normalization water quality parameters (HD = 169 mg/L, pH = 8.09, DOC = 4.94 mg/L) [38]. Due to its hardness and DOC concentration, it was concluded that this CMC and CCC would result in overestimates of hazard of Cu in Tai Lake [8].

The target water chemistry like based on the 5th, 10th, 20th or 50th centiles in water quality variables data sets corrected for hardness, pH and DOC was calculated. An example calculation for the HC_5 is given (Eq. 10).

$$\text{AcuteCu}HC_5 = \exp([0.29 \times \ln(DOC) + 0.555 \times \ln(HD) + 0.487 \times pH] - 3.46) \quad (10)$$

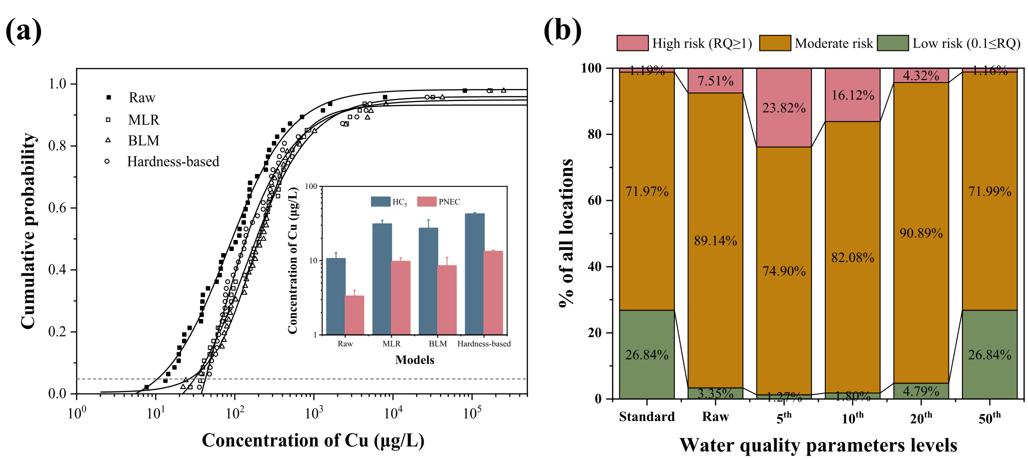

Fig. 3 Species sensitivity distributions of toxicity of Cu to aquatic organisms, normalized by the MLR, BLM and hardness-based models under standard water quality conditions and compared to the toxicity data without considering water quality parameters. The abscissa is the concentration value, and the ordinate is the calculated cumulative probability (**a**). Risk quotients of Cu in China under a standard water quality parameter level, and comparison to without considering water quality parameters, along with different water quality parameter values (**b**). MLR = multiple linear regression. BLM = biotic ligand model. Standard = toxicity data normalized based on the target water quality parameters suggested in Additional file 1: Table S3. Raw = raw toxicity data without considering the water quality parameters

where HD, DOC and pH are the target water quality parameters of interest.

The acute HC_5 of Cu was 6.57, 8.64, 14.20 and 31.58 μg/L under the 5th, 10th, 20th and 50th centiles of composite water quality parameter distribution, respectively. The AF that was used as the freshwater final acute-chronic ratio was 3.22 [15], and the PNEC values for Cu under the 5th, 10th, 20th and 50th centile water quality parameter values were 2.04, 2.68, 4.41 and 9.81 μg/L, respectively. At greater water hardness and concentrations of DOC, the toxicity of Cu was less, and a linear relationship was observed with hardness and DOC. Therefore, the calculated PNEC for Cu for lesser hardness and DOC conditions would more likely be protective of aquatic. When the target water chemistry was based on 20th centiles in water quality variables data sets only 5% locations were at greater risk; furthermore, it can cover approximately more than 99% sensitive water conditions (Fig. 3b).

Based on standard water quality parameter values, RQs for Cu ranged from 0.004 to 18.43. A total of 43 (1.19%) sites were defined as great risk, 2598 (71.97%) as moderate risk, and the numbers of high-risk sites were similar to the numbers of those concentrations exceeded the WQS to protect fishers. However, without considering water quality parameters, RQs for Cu ranged from 0.012 to 53.92, and 271 (7.51%) sites were defined as great risk, while 3,218 (89.14%) were defined as moderate risk (Fig. 3b). There was more than six times the percentage of high-risk sites with than under the standard water quality parameters.

Compared with the standard water quality parameter conditions, the RQs for Cu ranged from 0.02 to 87.70, while 860 (23.82%) sites were defined as great risk, and 2704 (74.90%) as moderate risk under the 5th centile water quality parameter conditions. When under the 10th centile water quality parameter conditions, the RQs for Cu ranged from 0.015 to 66.72, with 582 (16.12%) sites being defined as great risk, and 2,963 (82.08%) as moderate risk. RQs for Cu ranged from 0.009 to 40.60, with 173 (4.32%) sites defined as great risk, and 3,281 (90.89%) as moderate risk under the 20th centile water chemistry conditions. RQs for Cu ranged from 0.004 to 18.25, with 42 (1.16%) sites defined as great risk, and 2,599 (71.99%) as moderate risk under the 50th centile water chemistry. The toxicity of Cu in water to aquatic organisms is highly dependent on the different chemical speciation related to the water quality parameters such as hardness, pH and DOC; the result of RQs was changed in different water quality parameter conditions.

Results of prioritization indexes

China was divided into 15 regions. Median concentrations of Cu in the top 10 regions were 2.0 μg/L for YR and THL; 1.88 μg/L for DCL; 1.75 μg/L for HHR, HaiHR and CHL; 1.5 μg/L for YZR and PYL; and 1.25 μg/L for ZMR and DTL. RQ values based on standard water quality parameter conditions, comparison to raw toxicity data is shown in descending order. The greatest risk regions were YR, THL and DCL, based on the RQ values in standard water quality parameters, and this result was similar to that based on RQ values without considering water quality parameters (Fig. 4a). When considering both concentrations and frequency, the greatest risk regions were HaiHR, HHR and CHL, based on the standard water quality parameters conditions (Fig. 4c), and YR, DCL and HHR without considering water quality parameters (Fig. 4d).

Result of probabilistic ecological risk assessment

Results of MOS_{10} are shown (Fig. 5 and Additional file 1: Table S7). The 90th centile of exposure concentrations ($C_{0.9}$) of Cu was 3.21 μg/L, while the 10th centile toxicity date ($C_{0.1}$) of Cu was 12.85 μg Cu/L based on standard water quality parameters, and 5.04 μg Cu/L without correction for effects of water quality parameter. Furthermore, the 10th centile toxicity data ($C_{0.1}$) of Cu were 2.70, 3.55, 5.82 and 12.98 μg Cu/L at the 5th, 10th, 20th and 50th centile water quality parameter values. The proportion of sites that exceed thresholds for effects 10% of species ($C_{0.1}$) were 0.71% under the standard water quality parameter conditions and 2.81% under without correcting for decreases in bioavailability due to water quality parameters (Fig. 5a). Proportions of sites that exceeded the threshold for effects on 10% of species ($C_{0.1}$) were 16.52%, 6.22%, 2.47%, 0.71% under the 5th, 10th, 20th and 50th centile water quality parameter conditions (Fig. 5b). The proportion of sites that exceeded the threshold for effects on 10% of aquatic species ($C_{0.1}$) was 2.81% under without considering water quality parameter, which was less than toxicity data normalized in the 50th centile water quality parameter conditions, which was similar to the toxicity data normalized in the 20th centile water quality parameter conditions. In fact, most of toxicity data of Cu were collected from American laboratories and publications, and were collected under lesser hardness and DOC content water conditions.

Ecological risk assessment of Cu by use of the joint probability curves (JPCs) method, which can protect the complex ecosystems more accurately than RQs. JPCs result from a direct comparison of exceedance probability function between exposure concentrations data and toxicity concentrations data. Results of the JPCs

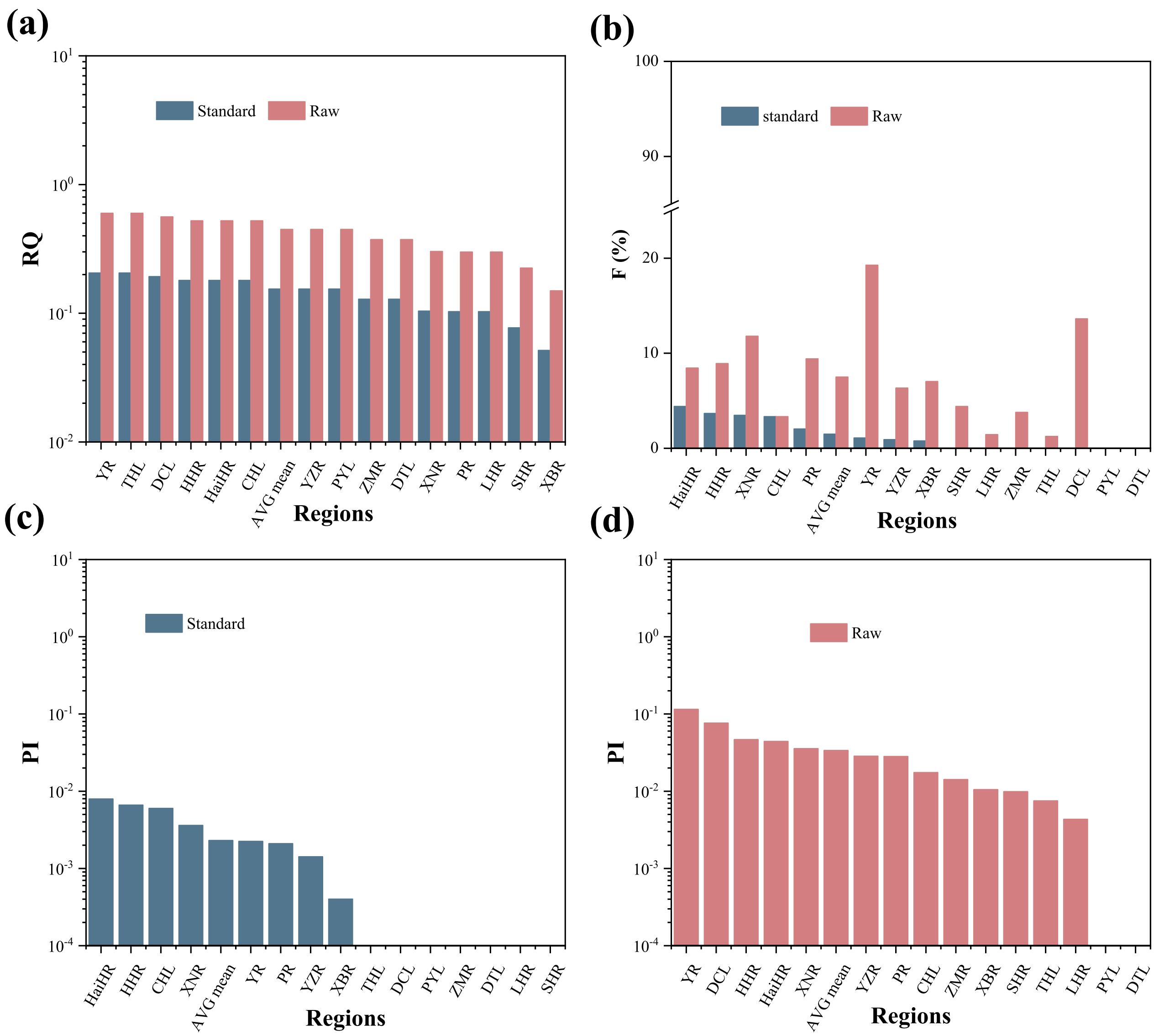

Fig. 4 Risk ranking of 15 regions for the median concentrations of Cu in surface waters and PNEC based on standard water quality parameter level, and comparison to the raw toxicity data (**a**); proportions (%) of concentrations exceeded PNEC in surface waters of China (**b**); and prioritized regions according to prioritization indexes in descending order based on the standard water quality parameter level and comparison to without considering water quality parameters (**c**, **d**)

indicated that the concentration of Cu in sites exceeding the threshold for effects to 10% of the species was 3.34% under the standard water quality parameter conditions, but 16.29% without correcting bioavailability for water quality parameters (Fig. 6a). Meanwhile, 52.71%, 39.58%, 19.26% and 3.25% of 3,610 sites exceeded the threshold for effects on 10% of the species under the 5th, 10th, 20th and 50th centile water quality parameter conditions (Fig. 6b).

With the preliminary risk quotients method, 1.19% of sites indicated a great risk under the standard water quality parameter conditions, only one-sixth of the percentage of sites with great risk that without considering water quality parameters (7.51% of sites indicated great risk). In method 2, considering both concentration and frequency, the greatest risk regions were the HaiHR, HHR and CHL, based on the standard water quality parameter conditions. Finally, a similar result in which the percentage of sites with great risk without considering water quality parameters was much greater than that under standard water quality parameter condition was indicated through probabilistic ecological risk assessment.

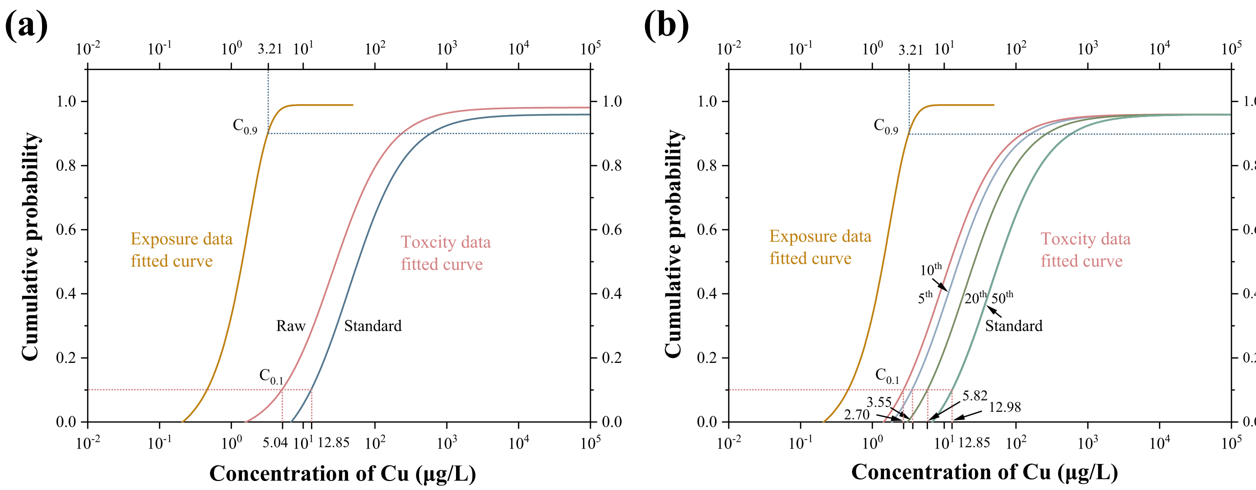

Fig. 5 ECD and SSD curves of Cu in surface water of China under different water quality parameter conditions: **a** standard water quality parameter condition compared with without considering water quality parameters; and **b** standard water quality parameter condition compared with considering different water quality parameter values. ECD = environmental exposure concentration. SSD = species sensitivity distribution

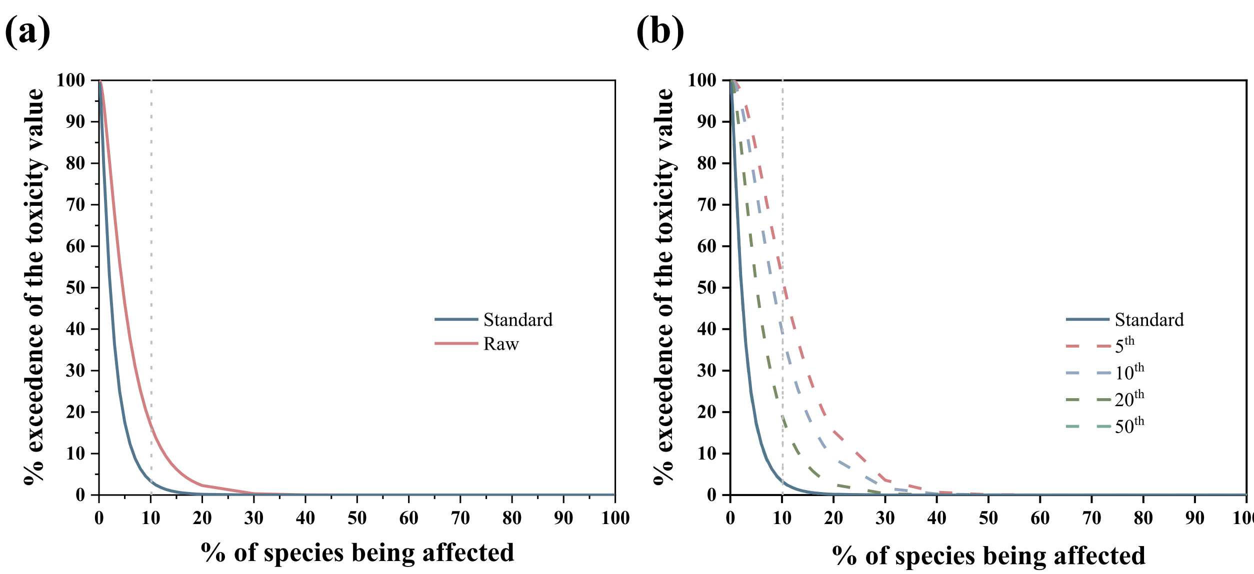

Fig. 6 Joint probability curves for ecological risk of Cu in surface water of China under different water chemistry distributions: **a** standard water quality parameter condition compared with without considering water quality parameters; and **b** standard water quality parameter condition compared with considering different water quality parameter values

Uncertainty analysis

Uncertainty in an ERA project is inevitable, even when employing higher-tier methods. Under natural conditions, water chemistry, such as hardness, pH and DOC, vary among seasons and geological regions and can influence bioavailability of metals, such as Cu. MLR models have been used to reduce or at lease describe uncertainty, but it cannot be completely avoided. Since the toxicity data sets of Cu, and the concentration data of Cu cannot represent all the results, the concentration data set of Cu was only collected during a period of two months. In the present study, according to our survey, studies have been reported chronic toxicity data were seldom descried other necessary parameters such as hardness, pH value, DOC, Ca, Ma, Na, K, SO_4^{2-}, Cl^- and alkalinity concentrations in aquatic ecosystems, for short of chronic toxicity, an assessment factor of 3.22 was used to construct PNEC. The ERA results can provide useful information for environmental managers and decision makers. However, it should be noted that neither the HQ ERA nor probabilistic ERA alone are as accurate as quantitative predictors of risk.

Conclusions

The mean concentration of Cu was 1.96 μg/L (ranging from 0.04 to 179 μg/L) in Chinese surface water, and the average concentrations of Cu in XNR, CHL, XBR and YR were higher than other regions. The MLR models and biotic ligand models have normalized toxicity data with similar precision in different ecological risk assessment. The PNEC of Cu was 9.71 μg Cu/L under the standard water quality parameters using MLR models of China but 3.28 μg Cu/L without considering water quality parameters. Based on the risk quotients method, ecological risk of Cu in XBR, XNR and DYR was greater than that of other regions, and there were six times of the percentage of greater-risk sites without considering water quality parameters than under the standard water quality parameter conditions. Considering both concentration and frequency, the greatest risk regions were HaiHR, HHR and CHL under the standard water quality parameters, but to YR, DCL and HHR without considering water quality parameters. Moreover, a similar result, in which the percentage of sites with high risk under standard water quality parameter condition was much higher than without considering water quality parameter, was indicated by the probabilistic ecological risk assessment method. In addition, comparing the results of risk assessment produced by three methods, and considering less than 5% sites (i.e., acceptable risk) were defined as high risk. We suggested that the 20th centile in water quality variables data sets (HD = 81 mg/L, pH = 7.29, DOC = 1.5 mg/L) as the normalization water quality parameters in sensitive areas, and calculated that the PNEC of Cu was 4.41 μg/L as a long-term HC_5 value for protection of aquatic organisms, especially spawning areas for fish.

Abbreviations

BLM	Biotic ligand model
DOC	Dissolved organic carbon
EC50	Median effect concentration
EQS	Environmental quality standard
HC5	Hazardous concentration for 5% species affected
HD	Hardness
HQ	Hazard quotients
JPC	Joint probability curve
MLR	Multiple linear regression
PI	Prioritization index
PNEC	Predicted no-effect concentration
RQs	Risk quotients
SSD	Species sensitivity distribution
US EPA	U.S. Environmental Protection Agency
WQC	Water quality criteria

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-023-00792-7.

Additional file1: Figure S1. Comparison of measured versus MLR-, hardness-based- and BLM-predicted for 9 species. **Figure S2.** Comparison of fitted models to derive the HC_5 based on MLR models. **Table S1.** Concentrations of total dissolved Cu in Chinese surface water of fifteen regions in 2021 (μg/L). **Table S2.** Water quality variables in Chinese surface freshwater of fifteen regions. **Table S3.** Suggestions of hardness, pH and DOC values for China, compared to previous works. **Table S4.** Species-specific multiple linear regression model coefficients. **Table S5.** Species-specific hardness-based model coefficients. **Table S6.** Raw and normalization of toxicity data for Cu. **Table S7.** The MOS_{10} of Cu in surface water of China under different water quality parameters condition. **Table S8.** Comparison of species-specific and pooled Cu MLR in Species and numbers of toxicity data to previous work. **Table S9.** Acute copper toxicity data used for normalization models development. **Table S10**. Hardness data source. **Table S11.** DOC data source.

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Author contributions

WL was the major contributor in experiments, data collection, analysis and manuscript writing. WL, CF and XJ designed the study. ZZ, YZ and WZ helped with the sample collection and analysis. HX and WL contributed to data collection. ZZ, Xiaowei Jin contributed to evaluation and manuscript writing. JPG contributed to improvements of the manuscript. All authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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