Environ Sci Pollut Res (2015) 22:4297–4304
DOI 10.1007/s11356-014-3655-4

RESEARCH ARTICLE

Derivation of marine water quality criteria for metals based on a novel QICAR-SSD model

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Received: 4 March 2014 / Accepted: 24 September 2014 / Published online: 8 October 2014

Abstract Establishment of water quality criteria (WQC) is one procedure for protection of marine organisms and their ecosystems. This study, which integrated two separate approaches, quantitative ion character–activity relationships (QICARs) and species sensitivity distributions (SSDs), developed a novel QICAR-SSD model. The QICARs predict relative potencies of individual elements while SSDs integrate relative sensitivities among organisms. The QICAR-SSD approach was applied to derive saltwater WQC for 34 metals or metalloids. Relationships between physicochemical properties of metal ions and their corresponding potencies for acute toxicity to eight selected marine species were determined. The softness index (σp) exhibited the strongest correlation with the acute toxicity of metals ($r^2>0.66$, $F>5.88$, $P<0.94\times10^{-2}$). Predictive criteria maximum concentrations for the eight metals, derived by applying the SSD approach to values predicted by use of QICARs, were within the same order of magnitude as values recommended by the US EPA (2009). In general, the results support that the QICAR-SSD approach is a rapid method to estimate WQC for metals for which little or no information is available for marine organisms.

Keywords Marine water quality criteria · Quantitative ion character–activity relationship · The softness index · Metals or metalloids · Species sensitivity distribution

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (doi:10.1007/s11356-014-3655-4) contains supplementary material, which is available to authorized users.

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Introduction

Oceans cover approximately 71 % of the Earth's surface and form its largest aquatic ecosystem with a great diversity of marine organisms. Due to industrialization and urbanization, quantities of metals have been mobilized into the marine environment, posing significant ecological risks on marine ecosystems, such as the extinction of some rare species, and reduction of biodiversity especially in coastal and estuarine areas (Johnston and Roberts 2009). To limit future contamination while remediating previous effects, countries, including China, are formulating effective protective measures for protecting the marine environment, and some useful progress has been made since the early 1960s (Goldberg 1992). Among the measures, derivation of marine water quality criteria (WQC) founded on scientifically sound environmental risk assessment framework is essential for regulating chemical discharges and water quality management as a tool to enhance protection of ecosystem structure and function (Leung et al. 2014; Merrington et al. 2014). With numerical WQC, environmental agencies and institutions can mount cost-effective monitoring programs, enforcing protective measures, designing remedial actions, and closely following international treaties to control pollution and protect marine biodiversity. Over the past few decades, some countries, such as the USA, Australia, New Zealand, Canada, China, and the Netherlands, and organizations, such as the European Union, have published or revised water quality criteria (US EPA 2009; ANZECC/ARMCANZ 2000; CCME 2007; Wu et al. 2010; Meng and Wu 2010; Feng et al. 2012a; Van Vlaardingen and Verbruggen 2007; ECB 2003). Since values recommended by US Environmental Protection Agency (US EPA) were taken as points of reference in our paper, a brief introduction about the history of marine WQC development in America is given. The US EPA has established comprehensive systems for deriving marine WQC and provided guidelines for development of individual national criteria over the past. Until now, marine WQC have been established for only 10 metals or metalloids by the US EPA (2009). Development of those criteria was based on toxicity data obtained from standard acute toxicity tests with surrogate, saltwater species that commonly inhabit the marine environment in North America. Attention has been focused primarily on protection of freshwater organisms in several developed and developing countries, such as China(Wu et al. 2008, 2011a, b; Feng et al. 2012b). Since fewer standard toxicity test methods or surrogate saltwater organisms are available, data, especially for toxicity of metals to saltwater vertebrates, have often been insufficient to meet requirements for developing WQC using conventional approaches (Merrington et al. 2014). Several studies have attempted to extrapolate toxicity data from freshwater to saltwater species (Hutchinson and Scholz 1998; Leung et al. 2001; Wheeler et al. 2002). However, there is currently no consensus on the reliability of these methods for derivation of WQC for protecting saltwater organisms using available toxicity data obtained from freshwater organisms.

Quantitative ion character–activity relationships (QICARs) establish intrinsic relationships between physicochemical properties and biological activities of metal ions, such as toxic potency to cause adverse effects on survival growth and reproduction. QICARs have been used as a robust statistical approach to develop predictive models of metal toxicity. Using data on toxicity of metals to the marine luminous bacterium *Vibrio fischeri* and the soil nematode *Caenorhabditis elegans*, Newman and his colleagues (McCloskey et al. 1996; Newman et al. 1998; Tatara et al. 1998; Ownby and Newman 2003) investigated the feasibility of predicting toxicity of metals based on physicochemical properties of metal ions. They found that the first hydrolysis constant $|\log K_{OH}|$ was strongly correlated with potency for toxic effects of metal ions (r^2=0.93). Multiple predictive equations were further established in combination with data from the US EPA's ECOTOX database, in which $|\log K_{OH}|$, together with the softness index σp, exhibited the strongest correlation with toxicities of metals (Ownby and Newman 2003). The softness index σp was found to be an optimal parameter for predicting toxicity of metals to *Tetrapymena pyriformis*. Mercury (Hg) and cadmium (Cd), which tended to bind with S-containing groups, were the most toxic to *T. pyriformis* (Bogaerts et al. 2001). QICARs have been used to predict effects of metals for which there were insufficient data on toxicity to a range of species to predict toxicity potency among different metals and among different species.

Therefore, this study developed and validated an alternative, novel, QICAR-SSD approach which integrates the QICARs to predict relative potencies among metals or metalloids with species sensitivity distributions (SSDs), which describe relative sensitivities among organisms to derive saltwater WQC. In accordance with US EPA requirements for derivation of saltwater WQC, eight families of marine species inhabiting North America were included in this study and there had to be sufficient toxicity data for each species. A QICAR model was then developed to predict acute toxicities of 34 metals or metalloids to selected sensitive marine species for which data were not available. The SSD approach, with the goal to protect 95 % of species, was used to predict criteria maximum concentrations (CMCs) of selected metals or metalloids. The QICAR-SSD model was then used to derive saltwater WQC. Comparisons between the predicted values and the CMCs recommended by the US EPA were also made as a way for validation of the QICAR-SSD approach.

Methods

Modeling data set

Toxicity data were selected for inclusion by application of basic requirements for data used in developing WQC, which have been previously described (Stephan et al. 1985). For instance, under those guidelines, a minimum of eight species (three phyla) were required. The specific rules are as follows: (1) the data set must include toxicity values for at least five metals to the same species, (2) the species must inhabit North America, (3) the toxicity tests must strictly follow standard methods, (4) the salinity of experimental water must be controlled within the range of 20–35‰, and (5) the exposure time of the acute toxicity test must be 48–96 h. Thus, five phyla and eight families of model aquatic organisms expected to be sensitive to the effects of heavy metals, including three Mollusca (*Mya arenaria*, *Crassostrea virginica*, *Nassarius obsoletus*), two Arthropoda (*Pagurus longicarpus*, *Mysidopsis bahia*), a Chordata (*Fundulus heterolitus*), an Annelida (*Nereis virens*), and an Echinodermata (*Asterias forbesi*), were considered (Calabrese et al. 1973; Eisler and Hennekey 1977; Lussier et al. 1985). Due to the paucity of data on acute toxicity of metals to marine organisms in the phylum Chordata, a single representative fish, the mummichog (*Fundulus heteroclitus*), was selected. The mummichog is a small euryhaline species that occurs in many places in the world and is often used in toxicity tests. Ecological classification of selected marine species, including phyla and species, is presented in Table 1.

Characteristics of metals and SSD fitting

As in previous studies (Wu et al. 2013; Mu et al. 2014), the following characteristics of metal ions establishing the QICAR model were considered: softness index, σp; the largest stability constant of complexes, $\lg\beta_n$; Pauling electronegativity, X_m; covalent index, X_m^2r; atomic ionization potential, AN/ΔIP; the first hydrolysis constant, $|\log K_{OH}|$; electrochemical potential, ΔE_0; atom size, AR/AW; relative softness of the ion, Z/rx (x is electronegativity); polarizable ability parameters, Z/r, Z/r^2, and Z^2/R; and the polarizable ability-like parameters, Z/AR and Z/AR^2 (Kaiser 1980; Lide and Haynes 2011; Pearson and Mawby 1967; Baes and Mesmer 1976; Wolterbeek and Verburg 2001).

The most significant characteristics of metal ions were selected based on correlations between ion characteristics and toxicity values. Selected ion characteristics were then used as independent variables, and toxicities of metals expressed as either 48 or 96 h LC_{50} were used as the dependent variables for five phyla and eight families of species by linear fitting. Predictive capacities of QICAR models were evaluated by use of the coefficient of determination (r^2), residual sum of squares (RSS), F value using multiple analysis of variance (ANOVA), and the level of type I error (P).

LC_{50} values were calculated for each marine species based on QICAR equations. According to the SSD analysis recommended by the US EPA, these toxicity data were sorted, fitted by the sigmoidal-logistic approach, then estimated the hazardous concentration for 5 % of species (HC_5) using OriginPro8 software (Wu et al. 2013). CMCs were obtained by halving the HC_5 values following the US EPA water quality criteria guidelines (Stephan et al. 1985).

Results and discussion

QICARs to predict the toxicity of 34 metals

Correlation analysis between log-LC_{50} and the 14 characteristics of metal ions demonstrated that the softness index σp is better correlated with log-LC_{50} (r^2>0.66). The σp, proposed based on the hard-soft-acid-base theory, is an evaluation parameter to comprehensively characterize the degree of difficulty for a metal ion to form covalent and ionic bonds (Jones and Vaughn 1978). Results of previous studies have indicated a correlation between toxicity and softness index of metal ions (Turner et al. 1983; McCloskey et al. 1996; Bogaerts et al. 2001). Therefore, here the σp was used to establish QICAR equations for eight model organisms by use of single-parameter linear regressions (Table 1).

The log-LC_{50} values of *F. heteroclitus* and *A. forbesi* are significantly positively correlated with σp (r^2=0.89, F=23.63, P=1.66×10^{-2}; and r^2=0.88, F=21.99, P=1.83×10^{-2}, respectively). Accuracy of prediction for *F. heteroclitus* was greater than that reported by Ownby and Newman (2003), who retrieved toxicity data pertaining to *F. heteroclitus* from the ECOTOX database and examined the correlation relationship between log-LC_{50} and $|\log K_{OH}|$ (r^2=0.78, F=14.51, P =1.90×10^{-2}). Log-LC_{50} values of bivalve mollusks *Mya arenaria* and *C. virginica* are also strongly correlated with σp (r^2=0.85, F=17.25, P=2.54×10^{-2}; and r^2=0.74, F=16.87, P=0.63×10^{-2}), whereas the Gastropoda *Nassarius obsoletus* of the same phylum has a P value of 5.60×10^{-2}. The toxicity data pertaining to the arthropod *P. longicarpus* and the annelid *Nereis virens* were weakly correlated with σp (r^2=0.66, F=5.88, P=9.38×10^{-2}; and r^2=0.70, F=6.98, P=7.75×10^{-2}, respectively). These three species have the P value, 0.05<P<0.10, accepted for statistical significance at the 90 % confidence level. Coefficients of determination (r^2) are all greater than 0.66, exhibiting a good prediction of metal toxicity (Table 1 and Fig. 1). As a reasonable model to predict acute toxicity value from the known

Table 1 One-variable regression model with σp

Species	Predicting equations	n	r^2	RSS	F	P	Data source
Mysidopsis bahia	Log 96 h-LC_{50}=(39.46±9.74) σp+(−3.67±1.04)	7	0.77	1.61	16.42	0.98×10^{-2}	Lussier et al. (1985)
C. virginica	Log 48 h-LC_{50}=(50.52±12.30) σp+(−4.73±1.33)	8	0.74	3.79	16.87	0.63×10^{-2}	Calabrese et al. (1973)
F. heteroclitus	Log 96 h-LC_{50}=(45.95±9.45) σp+(−1.97±0.96)	5	0.89	0.68	23.63	1.66×10^{-2}	Eisler and Hennekey (1977)
Mya arenaria	Log 96 h-LC_{50}=(49.83±12.00) σp+(−2.82±1.22)	5	0.85	1.09	17.25	2.54×10^{-2}	Eisler and Hennekey (1977)
A. forbesi	Log 96 h-LC_{50}=(57.81±12.33) σp+(−3.66±1.25)	5	0.88	1.15	21.99	1.83×10^{-2}	Eisler and Hennekey (1977)
P. longicarpus	Log 96 h-LC_{50}=(44.26±18.26) σp+(−3.09±1.85)	5	0.66	2.53	5.88	9.38×10^{-2}	Eisler and Hennekey (1977)
Nereis virens	Log 96 h-LC_{50}=(39.44±14.93) σp+(−2.34±1.51)	5	0.70	1.69	6.98	7.75×10^{-2}	Eisler and Hennekey (1977)
Nassarius obsoletus	Log 96 h-LC_{50}=(15.42±5.07) σp+(1.27±0.51)	5	0.76	0.20	9.25	5.58×10^{-2}	Eisler and Hennekey (1977)

r^2 is coefficient of correlation, RSS is residual sum of squares, and P is the statistical significance level

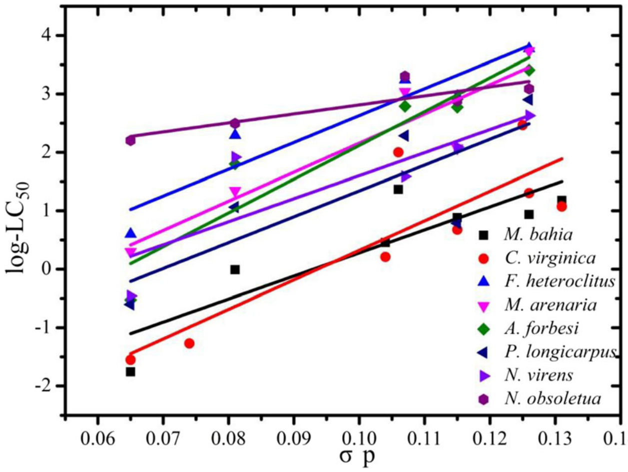

Fig. 1 Regression models of log-LC_{50} and softness index (σp) for eight model organisms

effects of tested metal, QICAR provides a potentially important field, both for academics and for those who are involved in setting water quality criteria for metals, especially data-poor metals.

Species sensitivity and HC_5 derivation

Based on the above QICAR equations, we obtain the log-LC_{50} values of each marine species for 34 metals or metalloids (Supplementary Table S2). It has been demonstrated that *C. virginica* and *Mysidopsis bahia* are more sensitive to metals than those of other phyla. *C. virginica* is most sensitive to Au, Hg, Ag, and Cd, whereas *Mysidopsis bahia* exhibited increasing sensitivity from soft to hard metals with log-LC_{50} values ranging from 0.16 to 3.55. These metals or metalloids belonged to IIA (Be, Mg, Ca, Sr, Ba), IIIA (Al, Ga, In, Tl), IVA (Ge, Sn, Pb), VA (As, Sb, Bi), IB (Cu), IIB (Zn), IIIB (Sc, Y, La), IVB (Ti), VB (V), VIB (Cr), VIIB (Mn), and VIII (Fe, Co, Ni) with the $\sigma p > 0.97 \times 10^{-1}$. This result is consistent with previous findings by Eisler and Hennekey (1997) and Snell et al. (1991). Eisler and Hennekey (1997) conducted investigations on toxicological hazards of selected heavy metals to representative marine species and exhibited that bivalve mollusks have the greatest sensitivity to Hg. Based on the comparative sensitivities for marine toxicity tests, *Mysidopsis bahia* appeared to be more sensitive to Pb than other species (Snell et al. 1991). Bivalves, especially the *Mytilus* sp., have been recognized as species more sensitive to Cu (US EPA 2003). In the present study, log-LC_{50} of *C. virginica* (0.52) was slightly greater than that of *Mysidopsis bahia* (0.44).

Besides, two bivalve mollusks, commonly served as marine pollution indicators, with different life stages are analyzed in this study, where *C. virginica* was at the embryonic development stage and *Mya arenaria* at the mature stage. The predicted LC_{50} values of *C. virginica* are significantly less than those of *Mya arenaria* (Supplementary Table S2*)*. Previously, it has been demonstrated that organisms had significantly greater sensitivities to toxicants in the embryonic and juvenile stages than in the mature stage. Juvenile *Ostrea edulis* were 1,000-fold more sensitive to Hg than were mature adults (Connor 1972).

Additionally, comparisons have been made between the predicted log-LC_{50} values and data from literature for those metals with few toxicity data. For Ca, for example, the 48-h excess log-LC_{50} of *Mysidopsis bahia* at salinity of 20‰ was 4.11 by Pillard et al. (2002), quite similar to the value predicted in this study (3.47). Thus, there is limited support for concluding that predicted CMCs based on these toxicity data would provide reference values for those metals without criteria value.

By using predicted acute toxicity values as the *x*-axis and cumulative probability as the *y*-axis, SSD plots of cumulative probabilities are used to calculate HC_5 values for 34 metals or metalloids (Fig. 2). These curves have r^2 of >0.91, F of $>1.13 \times 10^2$, and P of $<8.07 \times 10^{-5}$, which indicate a good fitting of the sigmoidal-logistic model (Supplementary Table S3). Log-HC_5 values of soft ions are less than those of boundary ions and hard ions. Specifically, soft ions, such as Hg, Ag, and Cd, have greater toxic potencies than boundary ions, such as Cu, Zn, Ni, and Pb, and hard ions, including Ca and Mg. These findings indicate that potencies of metal ions to cause toxicity are mainly attributed to their covalent binding with S- and N-containing groups in biological molecules. Results of previous studies have shown that binding constants for metal-ligand complexes, as well as the amount of metallothionein produced, were closely related to σp (Couillard et al. 1993; Zhou et al. 2011). Under the stress of exposure to harmful metals, soft ions, such as Hg and Cd, can rapidly

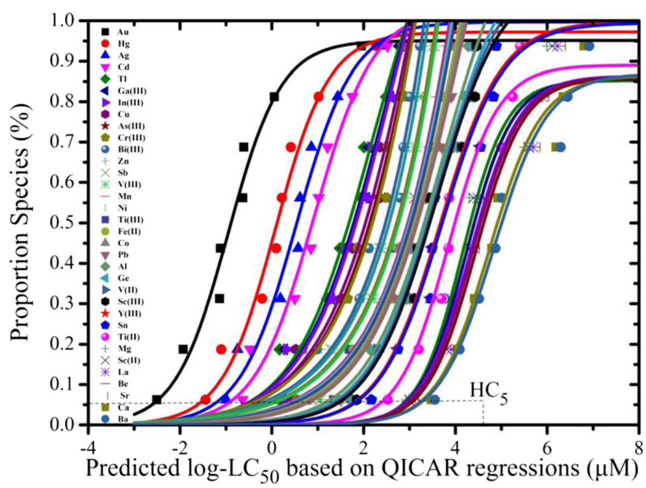

Fig. 2 Species sensitivity distribution analysis and derivation of the predicted log-HC_5 based on the QICAR regressions for 34 metals or metalloids. The predicted toxicities were derived from a minimum of eight species (three phyla), including *Mysidopsis bahia*, *C. virginica*, *F. heteroclitus*, *Mya arenaria*, *A. forbesi*, *P. longicarpus*, *Nereis virens*, and *Nassarius obsoletus*

bind with S-containing groups (−SH and C-SH) in biological organisms, further inducing the synthesis of metallothionein and reducing the enzyme activity or causing damage to structural proteins on the cytoplasm and cell membranes of organisms. Criteria maximum concentrations (CMCs) were recently derived for freshwater organisms by use of the QICAR-SSD model (Wu et al. 2013). The same ion characteristics were used in derivation of both freshwater and marine WQC. Predicted log-HC_5 values of 34 metals were strongly correlation with σp (Fig. 3, r^2=0.97, F=1.01×10^3, P=0.10×10^{-3}), which indicates that to some extent, it is feasible to derive WQC for marine organisms using the available toxicity data of freshwater organisms.

Validation and applicability of the QICAR-SSD model

QICAR-SSD models produced predicted CMCs for marine organisms, which were then compared with CMCs recommended by the US EPA for eight metals, and relative standard deviations between values predicted by use of the QICAR-SSD method and those for which values had been promulgated by the US EPA were as follows: Hg<Ni<Zn<As (III)<Ag <Cd<Cu<Pb. Deviations between predicted and promulgated values for Hg, Ni, Zn, As (III), and Ag were within a difference of 0.5 orders of magnitude, whereas those for Cd, Cu, and Pb are within a factor of 10 (Fig. 4). Acute toxicities of six metals, Hg, Cd, Cu, Zn, Ni, and Pb, to the crustacean *Neomysis integer* have been determined at different salinities. Values of the 96 h LC_{50} for Hg were almost the same at salinities ranging from 5 to 25‰; toxicities of Cd and Pb to *Neomysis integer* were significantly inversely proportional to salinity when compare to the effect of salinity on the toxicity of Ni, Cu, and Zn (Verslycke et al. 2003), which was consistent with our predicting error. The combined QICAR-SSD model provided weaker accurate prediction to metals with toxicity easily affected by salinity.

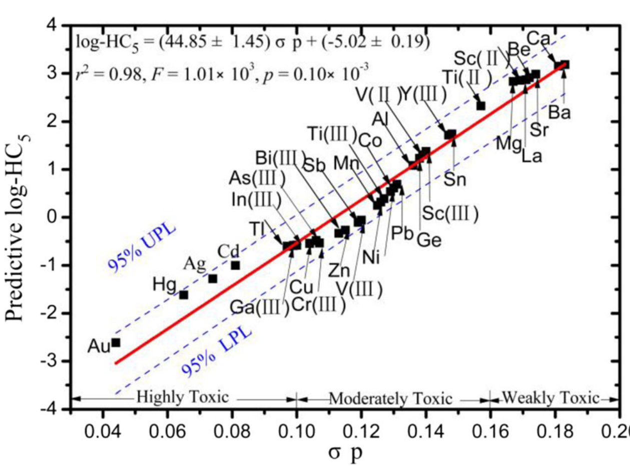

Fig. 3 The model for log-HC_5 and softness index (σp) at 95 % prediction level

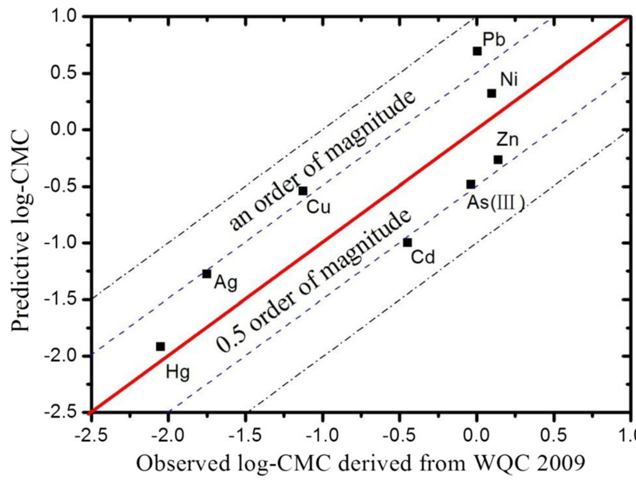

Fig. 4 The relationships between predicted log-HC_5 and recommended log-HC_5 derived from WQC

Environmental factors, such as salinity and dissolved organic matter, have been observed to have strong effects on the chemical speciation of Cd (Sunda et al. 1978; Endel and Fowler 1979). In derivation of WQC for Cd in seawater, effects of salinity on the toxicity of Cd to marine organisms were discussed. While the toxic effects of Cd on most aquatic species were found to be inversely proportional to salinity, others (Voyer 1975) have found different results when studying effects of salinity on toxicity of Cd to the small euryhaline fish, *F. heteroclitus*. Thus, salinity was not introduced as a correction factor in the development of WQC for Cd in seawater (US EPA 2001). For Cu, the predicted CMC was 9.19 μg/L, approximately twofold larger than the value recommended by the US EPA (4.8 μg/L). However, during the derivation of CMC for saltwater organisms in EPA, final acute value (FAV) was lessened from initially calculated value (12.3 μg/L) to 6.19 μg/L for protecting commercially and important mussel species (US EPA 2003). Consequently, a more accurate prediction of toxicity of Cu in seawater would be half of the calculated FAV. The QICAR-SSD model provided the least accurate prediction of toxicities of Pb, with a predicted value of 507 μg/L, which is greater than the recommended value (210 μg/L). The US EPA used 13 sets of toxicity data (nine invertebrate species and four fish species) for derivation of WQC for Pb in seawater. Of these, *F. heteroclitus* is the most sensitive species and has a significantly different sensitivity to Pb relative to the other three fish species (US EPA 1980). LC_{50} values for the other three fishes (*Cyprinodon variegatus*, *Menidia beryllina*, *Menidia menidia*) all exceeded solubility of Pb in seawater under the test conditions (3.14×10^3 μg/L, based on [Pb^{2+}] in $Pb(NO_3)_2$). Moreover, fish also demonstrate large variances during the derivation of water quality objective (WQO) for Pb in Hong Kong (HKEPD 2012). Yet, *F. heteroclitus* appeared to be less sensitive to other metals, like Cu and Cd, than those marine fish mentioned above ((US EPA 2003; Middaugh and

Dean 1977). Therefore, future studies need to better characterize the toxic effect and associated toxicity mechanisms of Pb on marine organisms.

Comparison of predicted freshwater and marine WQC

When a dual-parameter QICAR-SSD model was used to predict CMCs for metals in freshwater, CMCs for 25 metals or metalloids were within 1.5 orders of magnitude (Wu et al. 2013). WQC derived for marine systems were generally within 1 order of magnitude, thus improving the prediction accuracy of the QICAR-SSD model. For this reason, toxicity tests for seven model species were under the same condition. However, for certain metals, accuracy was less than that obtained by Wu et al. (2013). This is possibly due to complex interactions among multiple factors (form of metal, environment factors, condition of the targeted organism) in the marine environment (Bryan 1971). Metals, such as Pb, Cd, and Zn, which favor complexation with chloride at greater salinity, would have lesser concentrations of free ions of these metals. Alternatively, the ionic state has the greatest bioavailability and biological toxicity to aquatic organisms. Thus, these metals usually exhibit significant inverse relationships with salinity (Verslycke et al. 2003; Bielmyer et al. 2012). In contrast to these metals, inorganic complexation seems to have little importance in defining toxicity of Hg and Cu. Differences exist between their toxicity with the changing salinity. While acute toxicity of Hg is almost the same regardless of salinity, toxicity of Cu varied among salinities, probably by disrupting osmoregulation of the marine organism (Grosell et al. 2007; Adeyemi et al. 2012). This has challenged the prediction of metal toxicity to marine organisms using σp, which can only characterize the physicochemical properties of the metal itself.

Conclusions

Here, we have explored relationships between the marine acute toxicity endpoints (LC_{50}) and individual metal ion characteristics for 34 metals or metalloids. Using the resulting QICARs, acute toxicities of each metal in saltwater were used to develop a SSD for deriving 5 % hazard concentration (HC_5) values and CMCs for them. Then, we compared the predicted values with the eight published metal CMCs recommended by the US EPA (2009). Application of the QICAR-SSD method allows screening CMCs prediction for metals in saltwater with prediction errors within an order of magnitude. Thus, it might serve as a reference for the development of WQC for marine organisms in the absence of a CMC for metal and associated ecological-environmental risk assessment. Furthermore, there remains several points needing to be further developed: (1) Although it is not feasible to conduct toxicity testing for all species and conditions, more scientific data, especially of additional representative species, are needed for improving the prediction accuracy(Wu et al. 2012; Warne et al. 2014). (2) Salinity correction should be considered due to significant effect on the prediction accuracy. (3) The feasibility of QICAR-SSD model for prediction of chronic toxicity on marine organisms should be discussed in the next stage.

Acknowledgments The present study was supported by the National Basic Research Program of China (973 Program) (No. 2008CB418200), the National Natural Science Foundation of China (No.U0833603 and 41130743), and the National Water Pollution Control and Management Technology Major Projects of China (2012ZX07503- 003).

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Supplementary Material

Derivation of Marine Water Quality Criteria for Metals based on a Novel QICAR-SSD Model

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Number of pages: 4

Journal: Environ Sci Pollut Res

Table S1. log-LC_{50} of ten metal ions to eight taxonomic families used in regression models (μM)

Species	Cd	Cu	Pb	Hg	Ni	Ag	Zn	As(III)	Cr(VI)	Mn
M. bahia	-0.009	0.455	1.179	-1.758	0.937		0.883	1.366		
C. virginica		0.210	1.073	-1.554	1.303	-1.269	0.676	2.000		2.464
F. heteroclitus	2.292			0.601	3.776		2.963		3.243	
M. arenaria	1.347			0.300	3.737		2.071		3.040	
A. forbesi	1.800			-0.524	3.408		2.776		2.789	
P. longicarpus	1.063			-0.603	2.904		0.787		2.284	
N. virens	1.918			-0.457	2.629		2.093		1.585	
N. obsoletua	2.493			2.203	3.089		2.883		3.305	

Table S2. Acute toxicities of 34 metals or metalloids to representative species from eight taxonomic families

Metals	σp	*M.bahia*	*C.virginica*	*F.heteroclitus*	*M. arenaria*	*A.forbesi*	*P. longicarpus*	*N.virens*	*N.obsoletua*
Au	0.044	-1.932	-2.507	0.0570	-0.632	-1.118	-1.138	-0.608	1.950
Hg	0.065	-1.103	-1.446	1.022	0.415	0.096	-0.209	0.220	2.274
Ag	0.074	-0.748	-0.991	1.435	0.863	0.616	0.189	0.575	2.412
Cd	0.081	-0.472	-0.637	1.757	1.212	1.021	0.499	0.852	2.520
Tl	0.097	0.160	0.171	2.492	2.009	1.946	1.207	1.483	2.767
Ga(III)	0.099	0.239	0.272	2.584	2.109	2.061	1.296	1.561	2.798
In(III)	0.1	0.278	0.322	2.630	2.159	2.120	1.340	1.601	2.813
Cu	0.104	0.436	0.524	2.814	2.358	2.350	1.517	1.759	2.875
As(III)	0.106	0.515	0.625	2.906	2.458	2.466	1.605	1.838	2.906
Cr(III)	0.107	0.554	0.676	2.951	2.507	2.524	1.650	1.877	2.921
Bi(III)	0.113	0.791	0.979	3.227	2.806	2.871	1.915	2.114	3.014
Zn	0.115	0.870	1.080	3.319	2.906	2.986	2.004	2.193	3.045
Sb	0.119	1.028	1.282	3.503	3.105	3.217	2.181	2.350	3.106
V(III)	0.12	1.067	1.333	3.549	3.155	3.275	2.225	2.390	3.122
Mn	0.125	1.265	1.585	3.778	3.404	3.564	2.446	2.587	3.199
Ni	0.126	1.304	1.636	3.824	3.454	3.622	2.491	2.626	3.214
Ti(III)	0.127	1.344	1.686	3.870	3.504	3.680	2.535	2.666	3.230
Fe(II)	0.129	1.422	1.787	3.962	3.604	3.796	2.623	2.745	3.260
Co	0.13	1.462	1.838	4.008	3.653	3.853	2.668	2.784	3.276
Pb	0.131	1.501	1.888	4.054	3.703	3.911	2.712	2.824	3.291
Al	0.136	1.699	2.141	4.284	3.952	4.200	2.933	3.021	3.368
Ge	0.138	1.778	2.242	4.376	4.052	4.316	3.022	3.100	3.399
V(II)	0.139	1.817	2.293	4.422	4.102	4.374	3.066	3.139	3.415
Sc(III)	0.14	1.856	2.343	4.468	4.152	4.431	3.110	3.179	3.430
Y(III)	0.147	2.133	2.697	4.789	4.501	4.836	3.420	3.455	3.538
Sn	0.148	2.172	2.747	4.835	4.550	4.894	3.464	3.494	3.553
Ti(II)	0.157	2.527	3.202	5.249	4.999	5.414	3.863	3.849	3.692
Mg	0.167	2.922	3.707	5.708	5.497	5.992	4.305	4.244	3.846
Sc(II)	0.169	3.001	3.808	5.800	5.597	6.108	4.394	4.322	3.877
La	0.171	3.080	3.909	5.892	5.696	6.224	4.482	4.401	3.908
Be	0.172	3.119	3.960	5.938	5.746	6.281	4.526	4.441	3.923
Sr	0.174	3.198	4.061	6.030	5.846	6.397	4.615	4.520	3.954
Ca	0.181	3.474	4.414	6.351	6.195	6.802	4.925	4.796	4.062
Ba	0.183	3.553	4.515	6.443	6.294	6.917	5.013	4.875	4.093

Table S3. SSD fitting parameters and CMCs derived for 34 metals, with coefficient of determination, Chi-Sqr, *F* and *P* values.

Metals	***a***	***Xc***	***k***	***a*-SE**	***Xc*-SE**	***k*-SE**	**Chi-Sqr**	***Adj.r*^{2}**	***F***	***P***	**log-HC$_5$**	**AW**	**P-CMCs**	**CMCs**
Au	0.951	0.059	-0.950	0.110	1.739	0.305	0.00348	0.963	253.051	9.47×10^{-6}	-2.613	197	0.240	/
Hg	0.972	0.066	0.080	0.114	1.718	0.315	0.0033	0.965	266.952	8.29×10^{-6}	-1.616	201	2.431	1.8
Ag	0.997	0.086	0.542	0.146	1.617	0.331	0.00385	0.959	228.076	1.22×10^{-5}	-1.278	107	2.822	1.9
Cd	1.031	0.094	0.922	0.155	1.550	0.289	0.00294	0.969	299.017	6.26×10^{-6}	-0.999	112	5.617	40
Tl	1.392	0.403	2.169	0.529	1.187	0.280	0.00274	0.971	321.081	5.25×10^{-6}	-0.603	204	25.455	/
Ga(III)	1.551	0.617	2.446	0.729	1.122	0.290	0.00287	0.969	307.202	5.85×10^{-6}	-0.586	70	9.080	/
In(III)	1.658	0.795	2.608	0.877	1.089	0.298	0.00298	0.968	295.468	6.45×10^{-6}	-0.580	115	15.140	/
Cu	2.373	2.768	3.394	2.058	0.975	0.361	0.00399	0.957	220.466	1.33×10^{-5}	-0.542	64	9.186	4.8
As(III)	2.768	4.692	3.728	2.909	0.949	0.407	0.0048	0.949	182.868	2.11×10^{-5}	-0.484	75	12.297	69
Cr(III)	4.399	13.487	4.516	4.965	0.884	0.388	0.00438	0.953	200.693	1.68×10^{-5}	-0.533	52	7.614	/
Bi(III)	494.2	201760	10.89	502.4	0.819	0.364	0.00402	0.957	218.539	1.36×10^{-5}	-0.334	209	48.393	/
Zn	332.4	101629	10.53	379.5	0.815	0.404	0.0051	0.946	171.822	2.46×10^{-5}	-0.268	65	17.516	90
Sb	25.00	571.9	7.467	30.87	0.820	0.418	0.00567	0.940	154.621	3.19×10^{-5}	-0.108	51	19.904	/
V(III)	26.09	568.2	7.556	29.26	0.821	0.384	0.0048	0.949	182.743	2.12×10^{-5}	-0.059	51	22.274	/
Mn	5.153	12.979	5.490	3.953	0.883	0.270	0.00227	0.976	387.695	3.29×10^{-6}	0.250	55	48.915	/
Ni	4.110	7.544	5.189	2.973	0.903	0.262	0.00209	0.978	422.100	2.66×10^{-6}	0.319	59	61.491	74
Ti(III)	3.384	4.735	4.929	2.330	0.925	0.259	0.00199	0.979	443.511	2.35×10^{-6}	0.390	48	58.879	/
Fe(II)	2.469	2.245	4.506	1.582	0.977	0.266	0.002	0.979	440.533	2.39×10^{-6}	0.537	56	96.371	/
Co	2.170	1.663	4.334	1.355	1.007	0.277	0.0021	0.978	420.267	2.69×10^{-6}	0.613	59	120.963	/
Pb	1.938	1.280	4.186	1.181	1.039	0.290	0.00224	0.976	392.966	3.18×10^{-6}	0.690	207	507.178	210
Al	1.316	0.502	3.720	0.693	1.225	0.392	0.00349	0.963	251.772	9.59×10^{-6}	1.082	27	163.156	/
Ge	1.196	0.388	3.633	0.586	1.305	0.443	0.00417	0.956	210.913	1.49×10^{-5}	1.233	73	624.098	/
V(II)	1.151	0.348	3.605	0.544	1.344	0.470	0.00453	0.952	193.799	1.83×10^{-5}	1.305	51	515.241	/
Sc(III)	1.113	0.316	3.586	0.508	1.383	0.497	0.00491	0.948	178.544	2.24×10^{-5}	1.376	45	534.444	/
Y(III)	0.998	0.245	3.672	0.443	1.504	0.671	0.00775	0.917	112.515	6.97×10^{-5}	1.716	89	2314.408	/
Sn	0.995	0.249	3.705	0.456	1.498	0.693	0.00823	0.912	105.915	8.07×10^{-5}	1.744	119	3296.985	/
Ti(II)	0.890	0.116	3.853	0.229	1.849	0.784	0.00768	0.918	113.670	6.79×10^{-5}	2.326	48	5087.346	/
Mg	0.853	0.071	4.156	0.151	2.098	0.753	0.0066	0.930	132.413	4.67×10^{-5}	2.833	24	8166.035	/
Sc(II)	0.857	0.076	4.243	0.166	2.006	0.735	0.00692	0.926	126.264	5.25×10^{-5}	2.857	45	16183.130	/
La	0.864	0.084	4.338	0.189	1.896	0.717	0.00734	0.922	118.916	6.08×10^{-5}	2.867	139	51132.240	/
Be	0.861	0.08	4.371	0.180	1.908	0.695	0.007	0.925	124.899	5.39×10^{-5}	2.911	4	1628.283	/
Sr	0.859	0.074	4.444	0.169	1.908	0.652	0.00641	0.932	136.403	4.35×10^{-5}	2.984	88	42446.580	/
Ca	0.865	0.071	4.738	0.171	1.758	0.533	0.00538	0.943	162.871	2.81×10^{-5}	3.150	40	28276.780	/
Ba	0.870	0.073	4.831	0.179	1.697	0.509	0.00531	0.943	165.214	2.71×10^{-5}	3.183	137	104313.50	/