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Predicting criteria continuous concentrations of metals or metalloids for protecting marine life by use of quantitative ion characteristic–activity relationships–species sensitivity distributions (QICAR-SSD)

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ABSTRACT

Marine pollution by metals has been a major challenge for ecological systems; however, water quality criteria (WQC) for metals in saltwater is still lacking. Especially from a regulatory perspective, chronic effects of metals on marine organisms should receive more attention. A quantitative ion characteristic–activity relationships–species sensitivity distributions (QICAR-SSD) model, based on chronic toxicities for eight marine organisms, was established to predict the criteria continuous concentrations (CCCs) of 21 metals. The results showed that the chronic toxicities of various metals had good relationships with their physicochemical properties. Predicted CCCs of six metals (Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+}) were in accordance with the values recommended by the U.S. EPA, with prediction errors being less than an order of magnitude. The QICAR-SSD approach provides an alternative tool to empirical methods and can be useful for deriving scientifically defensible WQC for metals for marine organisms and conducting ecological risk assessments.

1. Introduction

With industrialization increasing in coastal cities, metal pollution of the marine environment, especially in estuaries and along coasts, has become a worldwide problem. To strengthen environmental management and to minimize impacts of metals on marine organisms, the U.S. EPA has recommended criteria continuous concentrations (CCCs) for 9 metals or metalloids in saltwater (arsenic (As), cadmium (Cd), hexavalent chromium (Cr(VI)), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se) and zinc (Zn)) since 1986. However, for other metals, CCCs are still lacking, which limits capabilities of government regulators to assess water quality and to make sound environmental management decisions. Thus, there was a need to derive CCCs for additional metals.

A CCC equals the highest concentration of a toxicant to which aquatic organisms can be exposed indefinitely without causing unacceptable effects. It is determined based on results of chronic toxicity tests (e.g. no observed effect concentrations (NOECs), lowest observed effect concentrations (LOECs) or maximum acceptable toxicant concentrations (MATCs)), but this information is not always easily obtained. Few standard methods for marine toxicity testing are available. In addition, systematic and comprehensive chronic tests of toxicity are costly and difficult due to challenges in maintaining constant toxic exposures and keeping control organisms alive and in good condition. Although use of an acute to chronic ratio (ACR) allows for an estimation of the chronic criteria from acute toxicity data, it was argued to have only a limited predictive value in aquatic ecosystems. Moreover, no ACR correlation was found across trophic levels (Ahlers et al., 2006). The biotic ligand model (BLM) is considered to be a promising method to estimate the activities of dissolved metals and has been used to derive water quality criteria (WQC) for copper in freshwater (U.S. EPA, 2007). However, there still remain limitations for extending the BLM from freshwater to saltwater (Arnold et al., 2005; Pinho and Bianchini, 2010). It has

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been recognized that in silico approaches have potential to become efficient alternative tools to empirical methods to drive WQC.

The quantitative ion characteristic-activity relationship (QICAR) is a mathematical method that is used to predict the biological activities of metal ions based on the assumption that similar electronic configurations should have similar functions. It can be expected to capture the relationships between the "microstructures" of metals, represented by physicochemical properties, and their macroscopic properties, such as biological toxicity, biosorption capacity or accumulation. Also, the QICAR approach is time- and cost-efficient and could reveal mechanisms of toxic potencies of metals. In the last few decades, extensive research has been conducted on QICAR to predict toxic potencies of metal cations (Khangarot and Das, 2009; McCloskey et al., 1996; Mendes et al., 2010; Newman and McCloskey, 1996; Ownby and Newman, 2003; Walker et al., 2007). The most common "descriptors" used in these studies are standard electrode potential (E_0), negative logarithm of the solubility product equilibrium constant (pK_{sp}), standard reduction-oxidation potential (ΔE_0), electronegativity (X, X_{AR}, or X_m) and softness index (σ_p). Additionally, QICAR combined with a species sensitivity distribution (SSD) approach has been used to predict WQC for protecting aquatic life (Chen et al., 2015; Mu et al., 2014; Wu et al., 2012), where linear regression analyses were employed to establish relationships between characteristics of metals and acute/chronic toxicities (log-LC_{50}, log-EC_{50} or log-NOEC) to eight families of selected organisms; the SSD approach was then performed to determine the water quality guidelines. However, there are still challenges in predicting the chronic WQC for metals in saltwater. First, marine ecosystems cover much broader trophic levels than do freshwater ecosystems, making it more difficult to select organisms that are typical, representative and sufficiently sensitive to be protective. Second, speciation and biosorption of metals in saltwater are more complex. Thus, it can be hard to find accurate descriptors. Third, only rarely are chronic experimental data published in the open literature.

This study attempted to predict the CCCs of metal ions for protection of marine life. Eight representative organisms (six phyla) with sufficient toxicity data were selected for deriving numerical WQC under the framework recommended by the U.S. EPA. The toxicity prediction model involves one input variable that describes the characteristics of metal ions. Chronic toxicities and CCCs were predicted by QICAR-SSDs. To validate predicted CCCs, they were compared with values recommended by the U.S. EPA. The QICAR-SSD model can be an alternative method to derive scientifically defensible WQC for metals for marine organisms and to conduct ecological risk assessment for which little or no empirical values are available.

2. Materials and methods

2.1. Modeling dataset

The chronic toxicity data used in the present study were taken from published literature (Table A.1). According to the U.S. EPA WQC guidelines, a minimum of eight species (three phyla) were required. Specific data screening rules are as follows: (1) All species selected here inhabit North America; (2) The toxicity data of at least five metals are available for each organism; (3) Chronic tests should cover an entire generation or reproductive life cycle. However, exposures during early, sensitive life stages of an organism are also included at times. However, those with mortality >20% in the control sample will be considered invalid; (4) All the toxicity tests should strictly follow the standard methods.

Eight marine species belonging to six phyla were used in this study, including an Echinoderm (*Paracentrotus lividus*), an Arthropod (*Americamysis bahia*), two Annelids (*Ctenodrilus serratus*, *Ophryotrocha diadema*), two Mollusks (*Ilyanassa obsolete*, *Mercenaria mercenaria*), a Chordate (*Cyprinodon variegatus*) and an Ochrophyte (*Skeletonema costatum*). Results of chronic toxicity tests were reported as NOEC, LOEC or MATC. However, considering the scarcity of chronic data, EC_{10} (effective concentration at 10% inhibition) of Ni^{2+} for *Cyprinodon variegatus* and *Skeletonema costatum* were converted into NOEC, by use of previously reported procedures (Durán and Beiras, 2013; Sijm et al., 2002).

2.2. Characteristics of metals and development of predictive relationships

There were 21 physicochemical characteristics of metal ions considered, involving atomic number (*AN*), atomic weight (*AW*), atomic radius (*AR*), Pauling ionic radius (r), ionic charge (Z), ionization potential (ΔIP), standard reduction-oxidation potential (ΔE_0), Pauling electronegativity (X_m), first-order hydroxide complex stability constant (log-$K_1(OH^-)$), logarithmic value of first hydrolysis constant ($|\log\text{-}K_{OH}|$), covalent index (X_m^2r), polarization force parameters (Z/r, Z/r^2 and Z^2/r), atomic ionization potential ($AN/\Delta IP$), softness index (σ_p), AR/AW radio, logarithmic value of the largest stability constant of complexes formed between the metal ion and EDTA, CN^- and SCN^- (log-β_n), relative softness (Z/rx) and similar polarization force parameters (Z/AR, Z/AR^2).

For each species, correlation analyses were conducted to investigate relationships between data on chronic toxicity and each characteristic of metals. The magnitude of association was tested using the F-statistic, with the level of significance set to $\alpha = 0.05$. Characteristics with the greatest predictive power were adopted to establish the predictive equations by a linear regression. The predictive potential of QICAR models were evaluated using the adjusted coefficient of determination ($Adj.r^2$), residual sum of squares (RSS), F value from the analysis of variance (ANOVA) and the p value. Meanwhile, internal validation (leave-one-out cross-validation, LOO_{CV}) was performed to assess robustness of predictive models and to limit over-fitting. Under leave-one-out cross-validation, N (the number of data points in the toxicity set) models were trained, each on a different combination of N-1 data points and tested on the remaining datum. The cross-validated correlation coefficient Q^2_{CV}, the sum of squared differences between observed and predicted toxicity, and the difference between r^2 and Q^2_{CV} were used as indicators for judging predictive power of models, with recommended reference criteria of $Q^2_{CV} > 0.6$ and $r^2\text{-}Q^2_{CV} \le 0.3$ (Eriksson et al., 2003).

2.3. SSD construction and HC_5 derivation

Chronic toxicities of each ion to eight representative organisms were predicted from QICAR equations and sorted in ascending order. Cumulative probabilities were then calculated for various species (Eq. (1)).

$$\text{cumulative probability} = (\text{rank}-0.5)/\text{number of species} \tag{1}$$

A Gumbel logistic approach (Gumbel, 1961; Gumbel, 1960) (Eq. (2)) was adopted for fitting functions for development of SSDs with the predicted log-C as the independent variable, while the cumulative probability was the dependent variable. Subsequently, the HC_5 of each metal ion, defined as the concentration to protect 95% species from hazard, was determined by the corresponding SSD equation and taken as the criteria continuous concentration (CCC) (Mu et al., 2014).

$$y = 1-e^{-e^{-\frac{x-a}{b}}} \tag{2}$$

3. Results and discussion

3.1. Predicting chronic toxicities of metals to eight marine organisms

Positive or negative relationships between the logarithmic value of the chronic toxic concentration (log-C) and 21 metal characteristics for each representative species were observed. Six descriptors, X_m, log-

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