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Comparative study of species sensitivity distributions based on non-parametric kernel density estimation for some transition metals☆

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ABSTRACT

Transition metals in the fourth period of the periodic table of the elements are widely widespread in aquatic environments. They could often occur at certain concentrations to cause adverse effects on aquatic life and human health. Generally, parametric models are mostly used to construct species sensitivity distributions (SSDs), which result in comparison for water quality criteria (WQC) of elements in the same period or group of the periodic table might be inaccurate and the results could be biased. To address this inadequacy, the non-parametric kernel density estimation (NPKDE) with its optimal bandwidths and testing methods were developed for establishing SSDs. The NPKDE was better fit, more robustness and better predicted than conventional normal and logistic parametric density estimations for constructing SSDs and deriving acute HC5 and WQC for transition metals in the fourth period of the periodic table. The decreasing sequence of HC5 values for the transition metals in the fourth period was Ti > Mn > V > Ni > Zn > Cu > Fe > Co > Cr(VI), which were not proportional to atomic number in the periodic table, and for different metals the relatively sensitive species were also different. The results indicated that except for physical and chemical properties there are other factors affecting toxicity mechanisms of transition metals. The proposed method enriched the methodological foundation for WQC. Meanwhile, it also provided a relatively innovative, accurate approach for the WQC derivation and risk assessment of the same group and period metals in aquatic environments to support protection of aquatic organisms.

1. Introduction

Transition metals in the fourth period of the periodic table include ten elements, i.e., scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn). These elements are widespread in aquatic environments and mostly can be hazardous when their concentrations are very small. For example, as one of the main pollutant of heavy metals in water, Cr has strong carcinogenic, teratogenic and mutagenic effects on aquatic species and human health (Friberg et al., 1979), of which general concentrations are from 1 to 10 μg/L in the freshwater and from 0.1 to 5 μg/L in the seawater (NAS, 1974). Ni could be highly accumulated and hazardous to human and aquatic organisms, especially when its ion bond with sulfate, could produce a variety of cancers. Cu, an essential trace element of organisms and human beings, is also a main pollutant in water, which mainly came from the industrial discharge and agricultural run-off, such as abuse of copper sulfate for the control of algae blooms.

Since the 1960s, the United States (U.S.) has worked on long-term water quality criteria (WQC) research for the purpose of protecting aquatic life and human health (U.S.EPA, 1985; U.S.EPA, 1986; U.S.EPA, 1999; U.S.EPA, 2002; U.S.EPA, 2004; U.S.EPA, 2006; U.S.EPA, 2009), and also many other countries and organizations, such as Australia, Canada, the European Union, Hong Kong, the Netherlands and New Zealand, have formulated and developed

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WQC guides to adapt their national or local environmental and ecological situations (Anzecc and Armcanz, 2000; CCME, 2007; ECB, 2003; Traas and De Bruijn, 2001; WHO, 2006; WHO, 2011). China also has managed its WQC based on ambient water quality standards recent years (Wu et al., 2010). WQC is the maximum acceptable threshold value under certain environmental conditions, which is recommended quantitative concentrations for chemical substances or environmental parameters for protecting specific water bodies functions and organisms from adverse effects (Meng and Wu, 2010; U.S.EPA, 1976; Zhang et al., 2010). In the latest guideline, United States Environmental Protection Agency (USEPA) recommended CMCs for only four transition metals (Cr, Ni, Cu and Zn), and CCCs for only five transition metals (Cr, Fe, Ni, Cu and Zn) in the fourth period of the periodic table for protecting aquatic life (U.S.EPA, 2012), but lack of Sc, Ti, V, Mn, Fe, Co, which mainly because the lack of data on toxic potencies.

Species sensitivity distribution (SSD) is a method that widely recommended by Australia, Canada, European Union, Hong Kong, the Netherlands, New Zealand and U.S. for the WQC derivation and risk assessment of the environment (Anzecc and Armcanz, 2000; CCME, 2007; ECB, 2003; Traas and De Bruijn, 2001; U.S.EPA, 1985). The method is based on the concept that different species for the same pollutant have different sensitivities could be described by use of a certain probability distribution function (Wu et al., 2013). If samples of species are sufficiently random and large that could be represent the community structure of a given ecosystem, the toxicity data would be used to develop the SSD for obtaining the acceptable hazardous concentration for 5% of species (HC5) and potentially affected fraction (PAF) of ecological risk (Posthuma et al., 2002). Based on the USEPA WQC methodology, the species used to derive WQC derivation need to contain a minimum eight species in three phyla (fish, zooplankton and benthic animals) (Stephen et al., 1985), which were at least 10 samples selected sufficiently randomly for obtaining an effective estimation to aquatic ecosystems (Wheeler et al., 2002). As the derivation results of SSDs, HC5 value is the foundation for the development of WQC (U.S.EPA, 2005; Van Straalen and Denneman, 1989). Meanwhile, predicted no effect concentration (PNEC) also could be calculated by use of the SSD and the entropy method for ecological risk assessment (Grist et al., 2002; Van Dam et al., 2012; Wang et al., 2008; Wheeler et al., 2002).

SSDs were widely applied to derive WQC for several transition metals, such as Cr (Du, 2012), Cu (Kong et al., 2011; Wu et al., 2011a), Mn (Kong et al., 2011), Ni (Du, 2012), Zn (Wu et al., 2011b), Cd (Kong et al., 2011; Wu et al., 2011c), and Hg (Kong et al., 2011; Wang et al., 2015a; Zhang et al., 2012), to protect freshwater aquatic organisms. SSDs are usually used in deriving HC5 and WQC of single organic pollutant or metal but rarely used to derive WQC for multiple pollutants (Campbell et al., 2000; Giesy et al., 1999; Solomon et al., 1996; TenBrook et al., 2010; Vardy et al., 2011). Commonly, parametric models used for developing SSDs and obtaining WQCs mainly include Burr Type III (Shao, 2000), Exponential Growth (Wu et al., 2012), Gaussian (Wu et al., 2011b), Gompertz (Newman et al., 2000), log-normal (Van Vlaardingen et al., 2004), log-logistic (Pennington, 2003), Sigmoid (Cao and Wu, 2010), and Weibull (Van Straalen, 2002). Not only parametric models, various non-parametric or free-distribution methods, such as Bootstrap (Newman et al., 2000), Monte Carlo (Posthuma et al., 2002), Bayesian methods (Hayashi and Kashiwagi, 2010), and non-parametric kernel density estimation (NPKDE) (Wang et al., 2015b) were also applied, which could describe the toxicity data more objectively and accurately since these methods can be processed without making such many assumptions as parametric methods. Bootstrap methods were first used to estimate HC5 values of pesticide by establishing SSDs (Jagoe and Newman, 1997). Liu et al. used both nonparametric approaches (Bootstrap and Bootstrap regression) and parametric approaches (Gompertz, Log-logistic, and Log-normal) to construct SSDs of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in assessments of ecological risk (Liu et al., 2014), and suggested that nonparametric methods were statistically superior to the parametric curve-fitting approaches.

In our previous study, we found that NPKDE does not need a *priori* information and depends on no overall distributions or parameters to describe, which could estimate unbiased characteristics of distribution only depended on sample data (Rosenblatt, 1956). The NPKDE was also verified its natural robustness in development of WQC for Zn, Cd and Hg of group IIB in the periodic table and compare with other jurisdictions (Wang et al., 2015b). The results showed that the NPKDE was better fit, more robustness and better predicted than conventional, parametric density estimations for establishing SSDs and convenient to compare with each other for WQC of same group of the periodic table. In addition, unlike bootstrap and bootstrap regression methods only can estimate the specific statistic value and relevant confidence interval using random resampling to establish specific parameter models or an empirical distribution function, the NPKDE could obtain the real cumulative density function (CDF) of all species (Grist et al., 2002).

The purpose of the present study was to investigate the toxicity differences of transition metals in the fourth period by use of SSD approach based on the NPKDE. Besides, optimal bandwidths and relevant test methods were also proposed. HC5s and WQC were obtained for nine metals based on SSDs as well. The hazard values were finally compared with different literature, which verified for accuracy and effectiveness of the NPKDE.

2. Methods and materials

2.1. Toxicity data sets

The present study selected all historical studies up to year 2014 that have reported acute toxicity data of ten metals in the fourth period from ECOTOX database by USEPA (http://cfpub.epa.gov/ecotox/). Accuracy and reliability of data were assessed by using standard approaches (Klimisch et al., 1997), which were based on requirements of WQC guidelines and literature (Zhang et al., 2012). The toxicity endpoint was lethality including LC50 or EC50. When there was more than one acute toxicity data at the same duration of exposure available for the same species, species mean acute values (SMAVs) were calculated by use of geometric means (Stephen et al., 1985). The study did not derive chronic HC5 and WQC, since after a review of all of the available literature, there was insufficient information on chronic effects on sub-lethal endpoints to construct chronic SSDs. Therefore, in all sections and terms the SSD used in the manuscript that refers to a SSD of EC50s/LC50s.

2.2. Modeling on SSDs

SSD is a probability distribution that describes different sensitivities of species, compounds or mixtures in a complex ecosystem, which is estimated from a toxicity data sample of various species and visualized as a cumulative distribution function (CDF) (Posthuma et al., 2002). Plotting positions of empirical cumulative probability of SSD were developed by *Hazen* for the first time (Equation (1)) (Cunnane, 1978).

$$p = \frac{i - 0.5}{n}, \quad 1 \le i \le n \tag{1}$$

where p denotes the cumulative probability, i is the sort level of