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Site-specific water quality criteria for lethal/sublethal protection of freshwater fish exposed to zinc in southern Taiwan

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HIGHLIGHTS

- Mg^{2+} is the most influential element to median effect concentrations of Zn exposure.
- Site-specific water quality criteria based on metal bioavailability in Taiwan are provided.
- High cation in rivers heavily decrease Zn bioavailability in the higher water effect ratios.

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ABSTRACT

There were considerable concerns about the zinc (Zn) pollution caused by electroplating, chemical, and computer-related high-tech industrial discharges in Kaohsiung Rivers situated at south Taiwan. There is, however, a lack of site-specific water chemistry based toxicity assessment and little is known about the sublethal toxicity on freshwater fish. This study proposes an integrated framework to link experimental and mechanistic model-based data analysis of lethal and sublethal Zn toxicities for grass carp (*Ctenopharyn odon idellus*) populations for providing the site-specific Zn water quality threshold in Kaohsiung Rivers. A biotic ligand model (BLM) that relates toxicity impairment of physiological active sites impacted by Zn species was used to elucidate the site-specific water chemistry affecting the bioavailability and biological response of grass carp exposed to Zn. Results indicated that 96-h LC50 for mortality and 28-d EC50 for growth inhibition were 474.7 ± 1.3 (mean ± SE) and 149 ± 23.5 μg L^{-1}, respectively. Here the BLM-based predicted steady-state LC50s for mortality were 2110.7, 818.2, 1303.6, 563.3, and 497.1 μg L^{-1}, whereas measured steady-state EC50s for growth inhibition were 726.8, 326.2, 373.4, 193.9, and 170.5 μg L^{-1} for the Agongdian, Houling, Love, Fengshan, and Gaoping Rivers, respectively. A positive correlation between Mg^{2+} and EC50 values were found in both acute ($r = 0.94$, $p < 0.01$) and chronic ($r = 0.97$, $p < 0.01$) Zn exposures. This study suggests that the use of site-specific water chemistry data and ecophysiological traits would enhance the predictive capacities to assess the potential effect of metal toxicity posed to aquatic organisms.

1. Introduction

Zinc (Zn) is naturally occurring in environment and is an essential micronutrient found in algae and fish (Genter and Lehman, 2000). The Zn contaminant is widely distributed in the air, water, and sediment resulted from the natural and anthropogenic sources, threatening the ecosystems. Recently, there were considerable concerns about the Zn pollution caused by electroplating, chemical, and computer-related high-tech industrial discharges in Agongtian River of Kaohsiung situated at south Taiwan (Taiwan EPA, 2013). In addition, Zn is the widely used materials in the anticorrosion treatment. The reported average Zn concentrations in aquaculture waters ranged from 0.06 to 0.13 mg L^{-1} in Taiwan (Liao and Chou, 2005). Doong et al. (2008) indicated that Zn concentrations ranged from 0.005 to 0.354 mg L^{-1} in Gao-ping River. However, Taiwan EPA (2013) reported that average Zn concentrations in Agongtian River were 32.4 and 21.8 mg L^{-1}, respectively, in 2011 and 2012, exceeding the water quality standard of 0.5 mg L^{-1}.

Zinc plays an essential role in cells and is the most abundant

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trace element in the most vertebrates (Eide, 2006). However, Zn would be toxic when it accumulated in excess of requirements. The adverse effect of Zn toxicity to freshwater fish is caused due majorly to the free Zn ion. Based on the toxicological principles in aquatic ecosystems, bioavailable Zn depends on the environmental and biological factors, whereas calcium, dissolved organic matter, and pH are the principle environmental factors affecting the Zn toxicity (Luoma and Rainbow, 2008; Lavoie et al., 2012; De Jonge et al., 2014). Thus, the knowledge of the major ion competition and complex effects on Zn species is dramatically important. In view of the biological factors, Zn toxicity to aquatic organisms were performed by two phases: (i) Zn accumulative capacity that is through absorption, distribution, metabolism, and excretion (i.e., toxicokinetics, TK), and (ii) accumulated Zn caused adverse effect that acts at the site of action or target site (i.e., toxicodynamics, TD).

Grass carp (*Ctenopharyn odon idellus*) is the most promising aquatic products because it is a commercially valuable and is one of major food sources for Taiwanese. Hence, it can be an ideal animal model used in this study as a bioindicator for waterborne Zn. Mortality is often a sensitive endpoint in chronic Zn exposure for freshwater fish (Abdel-Tawwab et al., 2011; Ezeonyejiaku and Obiakor, 2011; Calfee et al., 2014). However, little is known about the sublethal toxicity in grass carp. The sublethal endpoint of growth could be used to assess the movement and the reproduction (Anderson et al., 2001). If Zn levels in river and pond water elevated, it is likely to pose adverse effect on grass carp health, and even pose potential risk to peoples who consuming the grass carp.

Most studies focused only on the chemical influx without water chemistry conditions in studying the Zn toxicity (Pan and Wang, 2008; Javed, 2012). The biotic ligand model (BLM) has been developed intensively to account implicitly for the effect of water chemistry on the metal bioavailability. The BLM can be used to establish the site-specific environmental quality criteria and risk assessment framework (Lathour and Korre, 2015; McLaughlin, 2015; Rüdel et al., 2015). The EU Scientific Committee on Health and Environmental Risk has incorporated the BLM into the risk assessment framework (SCHER, 2007). Site-specific water chemistries affect the metal bioavailability and toxicity by considering both metal speciation (affected by pH, formation of organic and inorganic complexes) and competition between the major cations and the metal for binding to biotic ligand (BL) on the organisms. The BL is responsible for the transport of sodium, calcium or other ions associated with the transport ligand (Niyogi and Wood, 2004). It is important to take into account for integrating site-specific water conditions and bioavailability into a mechanistic framework on Zn toxicity in freshwater fish.

The objective of this study was to provide a framework to link experimental data and mechanistic model of lethal and sublethal toxicities in juvenile grass carp to provide the site-specific water quality criteria for Kaohsiung's rivers. Specifically, this study designed systematically the bioassays addressing the effects of Zn exposure on mortality and growth of grass carp populations. The essential bioassays, including lethal and sublethal toxicity tests, can be used to elucidate the Zn bioavailable active of TD mechanisms under Zn exposure in grass carp populations. Mechanistically, this study used the BLM to estimate bioavailable constants and to assess the water chemistry based Zn toxicity regarding the lethal and growth endpoint. Moreover, the accurate site-specific Zn water quality threshold in Kaohsiung's rivers can be further provided.

2. Materials and methods

2.1. Study area and sample collection

Water chemistry characteristics were collected from sampling stations situated at Agongdian, Houjin, Love, Fengshan, and Gaoping Rivers in Kaohsiung. The water samples were collected by using l L plastic bottle. The pH and dissolved oxygen (DO) were also measured *in situ*. The water samples were stored at 4 °C and were analyzed within 2 weeks.

2.2. Lethal toxicity bioassays

Juvenile grass carp were cultivated in the Department of Biomedical Science and Environmental Biology, Kaohsiung Medical University (Kaohsiung, Taiwan) and were considered to be uncontaminated by Zn. Juvenile grass carp kept with cool ice and adequate oxygen during transport to the laboratory. Upon arrivals, the fish were acclimated in tap water with dechlorinated at 25 °C with a 12 h light-dark cycle for at least 14 d before the initiation of exposure tests. Juvenile grass carp were fed daily once with the artificial food with pH value ranged from 7.6 to 7.8. Table 1 shows the acclimated water conditions. The chemical stock solution was prepared by dissolving a calculated amount of reagent-grade zinc chloride ($ZnCl_2$) in deionized water and the new stock solutions were prepared as needed during the toxicity tests. All experiments were carried out in 63 L (60 × 30 × 39 cm) indoor rectangular fiberglass aquaria in that DO in each tank was maintain at nearly saturation by aeration.

The lethal toxicity bioassays were conducted to obtain time-dependent median lethal concentration (LC50) values for juvenile grass carp exposed to various Zn concentrations. The experimental design and the lethal toxicity estimation are based on the well-established procedures given by Finney (1978) and Sparks (2000).

Twelve fish of a specific size class were selected randomly and transferred into each test aquarium. For each aquarium, an acute toxicity assay was conducted consisting of at least six treatments (control, 3, 6, 9, 21, and 27 mg L^{-1} Zn exposure groups) for 96 h. Gross mortality of fish to each concentration was recorded every 1 h for the first 12 h and every 2 h thereafter to the end of the experiment, and the dead fish was removed every 1–2 h. Fish were not feed throughout the test.

2.3. Sublethal toxicity bioassay

A 4-week sublethal toxicity bioassay was carried out to determine the toxic effects on grass carp growth inhibition responses. For each Zn concentration, 12 fish were exposed in one tank, respectively, with mean body length 11.4 ± 0.6 cm (mean ± SD) and mean body weight 13.9 ± 2.7 g wet wt. Dissolved oxygen (DO) in each tank was maintained at nearly saturation by aeration. Fish were fed once a day with commercial fish food at a rate of 1% grass body weight (either control or Zn exposures) at morning (1 h). Uneaten food was siphoned from the aquaria 30 min after feeding, and food was dried overnight and weighed. Mortality was

Table 1
Measured key water chemistry characteristics from laboratory and selected Kaohsiung rivers.

	pH	Temp. (°C)	DO (mg L^{-1})	Ion concentrations (mg L^{-1})		
				Na^+	Mg^{2+}	Ca^{2+}
Laboratory	7.78	25	9.558	8.244	18.683	4.45
Houjin River	7.52	30.5	8.57	7.2	43.81	8.24
Agongdian River	7.5	30.3	5.88	13.5	172.2	7.191
Love River	7.31	25	5.29	98.48	41.97	8.066
Fengshan River	7.51	32	7.56	10.74	17.29	9.343
Gaoping River	7.73	30	6.56	4.48	16.28	12.97