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Deriving freshwater quality criteria for copper, cadmium, aluminum and manganese for protection of aquatic life in Malaysia

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HIGHLIGHTS

- ▶ Toxicity tests were performed on eight freshwater species in Malaysia.
- ▶ Criterion Maximum Concentration (CMC) and Continuous Concentration (CCC) were derived.
- ▶ CMC values for Cu, Cd, Al and Mn are 1.3, 1.5, 488.9 and 39.1 μg L^{-1}, respectively.
- ▶ CCC values for Cu, Cd, Al and Mn are 0.3, 0.36, 117.8 and 9.4 μg L^{-1}, respectively.

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ABSTRACT

Freshwater quality criteria for copper (Cu), cadmium (Cd), aluminum (Al), and manganese (Mn) were developed with particular reference to aquatic biota in Malaysia, and based on USEPA's guidelines. Acute toxicity tests were performed on eight different freshwater domestic species in Malaysia, which were *Macrobrachium lanchesteri* (prawn), two fish – *Poecilia reticulata* and *Rasbora sumatrana*, *Melanoides tuberculata* (snail), *Stenocypris major* (ostracod), *Chironomus javanus* (midge larvae), *Nais elinguis* (annelid), and *Duttaphrynus melanostictus* (tadpole), to determine 96-h LC50 values for Cu, Cd, Al, and Mn. The final acute values (FAVs) for Cu, Cd, Al, and Mn were 2.5, 3.0, 977.8, and 78.3 μg L^{-1}, respectively. Using an estimated acute-to-chronic ratio (ACR) of 8.3, the value for final chronic value (FCV) was derived. Based on FAV and FCV, a Criterion Maximum Concentration (CMC) and a criterion Continuous Concentration (CCC) for Cu, Cd, Al, and Mn of 1.3, 1.5, 488.9, and 39.1 μg L^{-1} and 0.3, 0.36, 117.8, and 9.4 μg L^{-1}, respectively, were derived. The results of this study provide useful data for deriving national or local water quality criteria for Cu, Cd, Al, and Mn based on aquatic biota in Malaysia. Based on LC50 values, this study indicated that *R. sumatrana*, *M. lanchesteri*, *C. javanus*, and *N. elinguis* were the most sensitive to Cu, Cd, Al, and Mn, respectively.

1. Introduction

Metal contamination has been shown to have serious effects on both the environment and humans. Malaysia, as a developing country, is no exception, facing metal pollution caused especially by anthropogenic activities such as manufacturing, agriculture, sewage, and motor vehicle emissions (Shazili et al., 2006; DOE, 2009). Studies on metals in water and sediments indicate that some rivers in Malaysia were contaminated with As, Ag, Cd, Cu, Pb, and Zn, and some coastal sediments were contaminated by Pb, Zn and Cd (Shazili et al., 2006; DOE, 2009; Zulkifli et al., 2010; Yap and Pang, 2011). However, Malaysia has a lack of water quality criteria (WQC) based on local aquatic biota. The existing water quality standards (WQSs) for metals in Malaysia (National Water Quality Standards) are based mainly on foreign criteria or standards which have different environmental conditions compared to Malaysia. Many factors (physical, chemical and biological) are known to affect the toxicity of metals to aquatic organisms. These factors, especially the differences in taxonomic composition of Malaysian waters compared to those for which WQSs were developed, could result in foreign water quality criteria or standards that are over-protective or under-protective for aquatic ecosystems in Malaysia. In order to protect aquatic ecosystems in Malaysia, it is necessary to develop WQC for metals based on the responses of domestic aquatic biota with local environmental factors. This information could also be used to determine sensitive and potential organisms as bioindicators for metal pollution, especially in Malaysia.

Metals such as Cu, Cd, Al, and Mn are released from natural sources as well as human activity. Despite the adverse effect of metal on the environment and organisms, some metals are essential

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to living organisms. Mn plays an important role as an enzyme activator and component of metalloenzymes in the human body, while Cu is a functional part of the respiratory protein hemocyanin, combining with certain proteins to produce enzymes that act as catalysts to help a number of bodily functions (Rainbow, 2002). Toxicity testing is an essential tool for assessing the effect and fate of toxicants in aquatic ecosystems, and has been widely used as a tool to identify suitable organisms as a bioindicator and to derive water quality standards for chemicals (Adams and Rowland, 2003). Macroinvertebrates and fish as test organisms in toxicity tests have several valuable characteristics, such as their widespread distribution and common occurrence in freshwater, their ecological importance and ease of handling during testing, as well as their rapid growth, short life cycle and sensitivity to contaminants (Pascoe and Edwards, 1989; EPS, 1997). Therefore, these organisms have the potential to act as a bioindicator of heavy metals pollution in an aquatic environment and as organisms for toxicity testing. USEPA (1985) produced technical guidelines to give an objective way of deriving numerical national WQC. Acute-to-chronic ratios (ACRs) have been used extensively in ecological risk assessment to estimate the chronic toxicity of chemicals in aquatic organisms for which acute toxicity is known, but data regarding chronic toxicity are either limited or absent. The "final acute value" (FAV) is often divided by an acute-to-chronic toxicity ratio (ACR) to estimate a chronic criterion that would not result in unacceptable adverse effects to aquatic communities. Although the ACR approach has weaknesses for criteria development or risk assessment, a major strength of the ACR approach is that it allows estimates of chronic values for acutely sensitive species to be made for which no chronic data are available. In such cases, direct analysis of available chronic data may underestimate chronic toxicity, whereas the ACR allows some extrapolation of chronic effects for sensitive species, even though no chronic data exists (Mount et al., 2003).

In this study, freshwater WQC were developed for metals (Cu, Cd, Al, and Mn) based on their acute toxicity to freshwater fish and invertebrates using domestic aquatic organisms. The toxicity data for Cu, Cd, Al, and Mn were generated by conducting acute toxicity testing with eight fish and invertebrate species, and the Criterion Maximum Concentration (CMC) was derived. An estimated value of chronic data using an acute-to-chronic ratio (ACR) was used to derive the Criterion Continuous Concentration (CCC). The overall objective of this study was to provide useful data to derive national or local water quality criteria for Cu, Cd, Al, and Mn based on aquatic biota indigenous species in Malaysia.

2. Materials and methods

2.1. Organisms and test chemicals

In this study, eight local freshwater organisms have been used in toxicity testing, i.e. a prawn – *Macrobrachium lanchesteri*, two fish – *Poecilia reticulata* (guppy, family Poecillidae) and *Rasbora sumatrana* (family Cyprinidae), a snail (Gastropoda) – *Melanoides tuberculata* (family Thiaridae), an ostracod – *Stenocypris major*, a midge larvae – *Chironomus javanus* (Diptera, Chironomidae), an annelid – *Nais elinguis*, and a tadpole – *Duttaphrynus melanostictus*. *M. lanchesteri* and *R. sumatrana* were obtained from local pet stores. *P. reticulata*, *D. melanostictus* and *M. tuberculata* were collected from the field. *N. elinguis*, *S. major* and *C. javanus* were collected from a fishpond filter system. Prior to toxicity testing, the organisms were acclimatized for 1 week under laboratory conditions (28–30 °C with 12 h light:12 h darkness) in 20-L stocking tanks using dechlorinated tap water (filtered by several layers of sand and activated carbon; TC Sediment Filter® (TK Multitrade, Seri Kembangan, Malaysia)), and aerated through an air stone. During acclimation the organisms were fed with commercial fish food Tetramin® (Tetrawerke, Germany). Four metals were used in this toxicity testing: copper (Cu), cadmium (Cd), aluminum (Al), and manganese (Mn). The standard stock solutions (100 mg L^{-1}) of Cu, Cd, Al, and Mn were prepared from analytical grade metallic salts of $CuSO_4 \cdot 5H_2O$, $CdCl_2 \cdot 2½H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, and $MnSO_4 \cdot H_2O$ (Merck, Darmstadt, Germany). The stock solutions were prepared with deionised water in a 1-L volumetric container.

2.2. Acute toxicity test

Acute Cu, Cd, Al, and Mn toxicity experiments were performed for a 4-d period (96-h) using adult animals or larvae (fourth instar midge larvae and tadpole). Following a range-finding test, five Cu, Cd, Al, and Mn concentrations were chosen. Metal solutions were prepared by dilution of a stock solution with dechlorinated tap water. A control with dechlorinated tap water only was also used. The tests were carried out under static conditions with renewal of the solution every 2 d. Control and metal-treated groups each consisted of two to four replicates of five randomly allocated organisms. No significant stress was observed for the organisms in the solution indicated by 95–100% survival for the organism in the control water until the end of the study. For each species, a total of 10–20 animals per treatment (concentrations) were used in the experiment. Samples of water for metal analysis taken before and immediately after each solution renewal were acidified to 1% with ARISTAR® nitric acid (65%) (BDH Inc., VWR International Ltd., England) before metal analysis by a flame or furnace Atomic Absorption Spectrophotometer (AAS – Perkin Elmer (Massachusetts, USA), model – Analyst 800) depending on the concentrations. To avoid possible contamination, all glassware and equipment used were acid-washed (20% HNO_3 (Dongbu Hitek Co. Ltd., Seoul, Korea, 68%)), and the accuracy of the analyses was checked against blanks. Procedural blanks and quality control samples made from standard solutions for Cu, Cd, Al, and Mn (Spectrosol, BDH, England) were analyzed in every 10 samples in order to check for sample accuracy. Percentage recoveries for metals analyses were between 85% and 105%. Details of the experiments can be found in Shuhaimi-Othman et al. (2011a, 2011b, 2011c, 2012a, in press, 2012b).

During the toxicity test, organisms were not fed. The experiments were performed at room temperature of 28–30 °C, with a photoperiod of 12 h light:12 h darkness using fluorescent lights (334–376 lux). Water quality parameters (pH, conductivity, and dissolved oxygen) were measured every 2 d using portable meters (model-Hydrolab Quanta®, Hach, Loveland, USA); water hardness samples were fixed with ARISTAR® nitric acid and measured by a flame atomic absorption spectrophotometer (AAS – Perkin Elmer Analyst 800). Mortality was recorded every 3–4 h for the first 2 d and then at 12- to 24-h intervals throughout the test period. Any dead animals were removed immediately.

2.3. Statistical analyses and data integration

Median lethal concentrations (LC50) for the animals exposed to Cu, Cd, Al, and Mn were calculated using measured metal concentrations. FORTRAN programs based on the methods of Lichfield (1949) and Lichfield and Wilcoxon (1949) were used to compute the LC50. Interpretation of toxicity data was conducted according to the methods described in the guidelines of USEPA (1985). Final acute value (FAV) was derived using the FAV equation in the guidelines. The criteria maximum concentration (CMC) was the FAV divided by two. To obtain the final chronic value (FCV), the FAV was divided by the ACR. ACRs have been used to estimate chronic toxicity for chemicals and species with known acute toxicity but