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Deriving freshwater safety thresholds for hexabromocyclododecane and comparison of toxicity of brominated flame retardants

Liang Dong[a,*], Lei Zheng[b,c], Suwen Yang[b], Zhenguang Yan[b], Weidong Jin[b], Yuhong Yan[b]

[a] National Research Centre for Environmental Analysis and Measurement, Beijing100029, China
[b] State Key Laboratory of Environmental Criteria and Risk Assessment, Lake Research Center of Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[c] College of Water Science, Beijing Normal University, Beijing 100875, China

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ABSTRACT

Hexabromocyclododecane (HBCD) is a brominated flame retardant used throughout the world. It has been detected in various environmental media and has been shown toxic to aquatic life. The toxic effects of HBCD to aquatic organisms in Chinese freshwater ecosystems are discussed here. Experiments were conducted with nine types of acute toxicity testing and three types of chronic toxicity testing. After comparing a range of species sensitivity distribution models, the optimal model of Bull III was used to derive the safety thresholds for HBCD. The acute safety threshold and the chronic safety threshold of HBCD for Chinese freshwater organisms were found to be 2.32 mg/L and 0.128 mg/L, respectively. Both values were verified by the methods of the Netherlands and the United States. HBCD was found to be less toxic compared to other widely used brominated flame retardants. The present results provide valuable information for revision of the water quality standard of HBCD in China.

1. Introduction

Hexabromocyclododecane (HBCD) is an emerging brominated flame retardant which is widely used throughout the world. It was used in many manufactures, especially in polystyrene foam, indoor decoration, textiles, and electronic products. In the year of 2001, the global demand for HBCD was up to 16,700 t. In Europe, this figure was 9500 t (Alaee et al., 2003; Covaci et al., 2006). The production capability of HBCD in China amounted to approximately 7500 t/y (Wang et al., 2010). HBCD was detected in fish and sediment samples from the Viskan River in Sweden in 1998 for the first time (Sellström et al., 1998). Up to now, it has been detected in various environmental media, such as air, soil, water and organisms in Europe, Asia, North and South America, and even the Arctic (Abdallah et al., 2007; De Wit et al., 2006; Johnson Restrepo et al., 2008; Jun et al., 2009; Kakimoto et al., 2008; Remberger et al., 2004; Verreault et al., 2005).

Currently, the high detection rate, widespread use, long half-life, and pronounced toxicity of HBCD have drawn attention from both scientific and regulatory communities. HBCD has significant ecotoxicity to aquatic organisms, such as the hepatotoxicity, neurotoxicity and endocrine toxicity (Palace et al., 2008; Wang et al., 2011; Wu et al., 2008), and may pose risks to aquatic ecosystems. However, a comprehensive ecological risk assessment of HBCD is difficult to perform because of the absence of safety thresholds for HBCD. Safety thresholds are of great importance in the water environment management because it supports the establishment of water quality standards and could be used as a tool to assess the risk level. The establishment of safety thresholds for emerging contaminants has become a research hotspot in China (Wang et al., 2013; Yan et al., 2012; Yin et al., 2003).

The aim of this study was to (1) obtain the acute and chronic toxicity data of HBCD to Chinese freshwater organisms, (2) optimize the suitable model for safety threshold derivation, and (3) assess the ecological risks of HBCD in the water environment. Nine acute toxicity tests and three chronic tests were performed using 9 Chinese resident species, and the safety thresholds including the acute safety threshold and the chronic safety threshold of HBCD for freshwater aquatic organisms were derived based on species sensitivity distribution (SSD) model (Dyer et al., 2008; Raimondo et al., 2007; Wu et al., 2012). Only when an emergency pollution accident occurs, the acute safety threshold is used to assess the environmental risk of waterbodies in a short time. The chronic safety threshold is used to assess the environmental risk in the daily management of water environment. The ecological risk of HBCD in some water basins was also assessed compared to the derived safety thresholds. In this way, the present

* Corresponding author.
E-mail address: dongliang613@126.com (L. Dong).

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work would provide valuable information for pollution management of HBCD exposure in ambient water environment.

2. Materials and methods

2.1. Ethics statement

The Animal Care and Use Committee (ACUC) in the Chinese Research Academy of Environmental Sciences (CRAES) approved this study. All studies were strictly performed in accordance with the guidelines of the ACUC. We tried our best to minimize the suffering to the aquatic lives during the toxicity test period, and all living organisms were euthanized after the test. In addition, *Bufo gargarizans*, one of the test organisms, were obtained from Beijing Olympic Park with the permission of the administration office of the park. Here, we guaranteed that all species used in this study did not include endangered or protected species.

2.2. Test chemicals and organisms

Firstly, 50 mg/mL stock solution was prepared with analytical grade HBCD (99%) and DMSO co-solvent purchased from J & K Chemical. Tap water was dechlorinated with activated carbon and used for dilution testing. Dilution water quality parameters were as follows: pH 7.0 ± 0.5, dissolved oxygen (DO) 7.0 ± 0.5 mg/L, total organic carbon 0.02 mg/L, and hardness 190 ± 0.1 mg/L as $CaCO_3$. M4 medium was the growth media of algae. A liter of the medium consisted of 294 mg $CaCl_2·2H_2O$, 123 mg $MgSO_4·7H_2O$, 5.8 mg KCl, 64.8 mg $NaHCO_3$, 10 mg $Na_2SiO_3·9H_2O$, 0.274 mg $NaNO_3$, 0.143 mg KH_2PO_4, 0.184 mg K_2HPO_4, 2.86 mg H_3BO_3, 0.996 mg $FeSO_4·7H_2O$, 0.361 mg $MnCl_2·4H_2O$, 0.306 mg LiCl, 0.071 mg RbCl, 0.152 mg $SrCl_2·6H_2O$, 0.016 mg NaBr, 0.063 mg $Na_2MoO_4·2H_2O$, 0.0168 mg $CuCl_2·2H_2O$, 0.013 mg $ZnCl_2$, 0.010 mg $CoCl_2·6H_2O$, 3.25 μg KI, 2.19 g Na_2SeO_3, 0.575 g NH_4VO_3, 2.50 mg $Na_2EDTA\ 2H_2O$, 75 μg thiamine HCl, 1.0 g cyanocobalamin (vitamin B12) and 0.75 g biotin (Abe et al., 2001).

According to the guidelines of Netherland, European Union (EU), Canada and United States (USA) (CCME., 2007; ECE, 2003; RIVM, 2007; Stephen et al., 1985), the toxicity data used to develop the safety thresholds were collected from eight native freshwater aquatic animals and one aquatic plant. In this study, they were crucian carp (*Carassius carassius*), topmouth gudgeon (*Pseudorasbora parva*), Asiatic toad tadpole (*Bufo gargarizans)*, water flea (*Daphnia magna*), freshwater shrimp (*Macrobrachium nipponense*), chironomid larvae (*Chironomus plumosus*), tubifex (*Limnodrilus hoffmeisteri*), mudsnail (*Cipangopaludina cathayensis*), and four-tailed scenedesmus (*Scenedesmus quadricauda*). Each organism was acclimated in the laboratory for at least seven days before toxicity tests, which was in accordance with ASTM guidelines (ASTM, 1993a; b, c, 2012, 2014).

2.3. General test conditions

Formal test concentrations were determined after preliminary experiments. Acute toxicity tests were developed using a static test, while the chronic toxicity test was semi-static. Each vessel contained ten organisms (excluding *Daphnia magna* chronic toxicity test), and the blank controls and co-solvent controls were also designed according to the test guidelines. HBCD concentrations were monitored throughout the test. Experimental temperature was maintained at 22 ± 2 °C. Photoperiod was 12 h:12 h. Temperature, DO, and pH were measured daily for the acute toxicity tests and twice a week at least for the chronic toxicity tests. Each observed results were recorded at least once per day. The toxic endpoint in acute toxicity tests was 48-h-EC_{50} for *Daphnia magna*, 96-h-LC_{50} for other animals, and 96-h-EC_{50} for *Scenedesmus quadricauda*. EC_{10} was the toxic endpoint for the most sensitive indicator in the chronic toxicity test. The mortality rate of organisms in the blank control and co-solvent control groups was below 10%.

2.4. Acute toxicity tests

2.4.1. Carassius carassius acute toxicity test

Carassius carassius were purchased from the Spring Flower Market in Chaoyang District, Beijing. These fish had an average weight of 6.0 ± 0.8 g and average length of 7.0 ± 0.5 cm. Besides a clean water control and a solvent control, there were six test groups in the formal experiments with concentrations at 160, 224, 313, 439, 615, and 861 mg/L. The toxicity tests were conducted in three replicates at each clean water control, solvent control (DMSO) and the assigned concentrations.

2.4.2. Bufo gargarizans acute toxicity test

Bufo gargarizans were acquired from Beijing Olympic Park. Average weight was 0.48 ± 0.05 g, and average length was 1.8 ± 0.2 cm. Besides a clean water control and a solvent control, there were six test groups in the formal experiments with concentrations at 40, 68, 116, 197, 334, and 568 mg/L. The toxicity tests were conducted in three replicates at each clean water control, solvent control (DMSO) and the assigned concentrations.

2.4.3. Daphnia magna acute immobilization toxicity test

Daphnia magna (age < 24 h) were obtained from CRAES. *Daphnia magna* were exposed in 200 mL beaker containing 100 mL of testing liquid, and the exposure time was 48 h. Besides a clean water control and a solvent control, there were six test groups in the formal experiments with concentrations at 8, 12, 18, 27, 41, and 61 mg/L. The toxicity tests were conducted in three replicates at each clean water control, solvent control (DMSO) and the assigned concentrations. The endpoint was EC_{50} based on immobilization. *Daphnia magna* that was not able to swim within 15 s after gentle agitation of the test vessel was considered to be immobilized (even if they could still move their antennae).

2.4.4. Macrobrachium nipponense acute toxicity test

Macrobrachium nipponense were purchased from Beijing Dahongmen Aquatic Product Market. Average weight was 0.3 ± 0.05 g, and average length was 4 ± 0.2 cm. Besides a clean water control and a solvent control, there were six test groups in the formal experiments with concentrations at 6, 7.8, 10, 13, 17, and 22 mg/L. The toxicity tests were conducted in three replicates at each clean water control, solvent control (DMSO) and the assigned concentrations.

2.4.5. Chironomus plumosus acute toxicity test

Chironomus plumosus were purchased from Vast Forest flower Market in Beijing. Average weight was 0.05 ± 0.01 g, and average length was 1.2 ± 0.2 cm. *Chironomus plumosus* were exposed in a 90 mL petri dish containing 10 mL of test liquid for 96 h. Besides a clean water control and a solvent control, there were six test groups in the formal experiments with concentrations at 450, 540, 648, 778, 934, and 1120 mg/L. The toxicity tests were conducted in three replicates at each clean water control, solvent control (DMSO) and the assigned concentrations.

2.4.6. Limnodrilus hoffmeisteri acute toxicity test

Limnodrilus hoffmeisteri were purchased from Vast Forest flower Market in Beijing. Average weight was 0.03 ± 0.01 g, and average length was 0.8 ± 0.2 cm. *Limnodrilus hoffmeisteri* were exposed in a 90 mL petri dish containing 10 mL of test liquid for 96 h. Besides a clean water control and a solvent control, there were six test groups in the formal experiments with concentrations at 150, 225, 338, 506, 759, and 1140 mg/L. The toxicity tests were conducted in three replicates at each clean water control, solvent control (DMSO) and the assigned concentrations.