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Deriving the freshwater quality criteria of BPA, BPF and BPAF for protecting aquatic life

Lei Wang[a,b], Zhen Wang[b], Jining Liu[b], Guixiang Ji[b], Lili Shi[b], Jing Xu[b], Jiaxin Yang[a,*]

[a] College of Life Sciences, Nanjing Normal University, Nanjing 210023, China
[b] Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, China

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ABSTRACT

Bisphenol A (BPA) has been recognized by the European Chemicals Agency (ECHA) as an endocrine disruptor, and its use in thermo paper has been restricted from 2020 under the Regulation concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). However, substances with similar structures such as bisphenol F (BPF) and bisphenol AF (BPAF) are widely used as BPA substitutes and commonly detected in aquatic environments. In this study, the water quality criteria of BPA, BPAF and BPF for protecting the aquatic life were derived to provide safety thresholds for their environment risk management. To accomplish this, the species sensitivity distribution (SSD) method was applied based on ecotoxicity data available in the literature and the supplementary toxicity test results for BPF and BPAF towards *Marisa cornuarietis*, *Chironomus tentans* and *Scenedesmus obliquus*. When compared with BPF, BPAF was found to be more acutely and chronically toxic to *Marisa cornuarietis, Chironomus tentans* and *Scenedesmus obliquus*, among which *Chironomus tentans* showed the most sensitivity. The criteria maximum concentrations (CMCs) of BPA, BPF and BPAF were derived to be 520, 227, and 43.4 $\mu g \cdot L^{-1}$, while the criteria continuous concentrations (CCCs) were 7.50, 54.0 and 26.4 $\mu g \cdot L^{-1}$, respectively. These findings indicate that BPA, BPF and BPAF posed negligible risks in typical rivers and lakes with available exposure concentrations because their measured concentrations are below their CCCs.

1. Introduction

Bisphenol A (BPA) is an organic chemical raw material used in plasticizers, flame retardants, antioxidants, heat stabilizers, rubber antioxidants, pesticides, paints and other fine chemical products, as well as in the production of many consumer products, including food containers, paper products (e.g., thermal receipts), pipes, toys, medical equipment, and electronics (Van den berg et al., 2007). Many studies have documented the adverse effects of BPA on reproduction and development, neural networks, and cardiovascular, metabolic and immune systems in in vitro assays and laboratory animal studies (European Chemicals Agency (ECHA), 2017). Given the widespread exposure of BPA to humans and the many health risks it poses, the European Union (EU) and Canada banned its use in baby bottles in 2010 and 2011, respectively (Chen et al., 2016). The stringent regulations and public concern regarding BPA have stimulated development and production of alternative substances. Some BPA analogs, such as BPF and BPAF, which share a common structure of two hydroxyphenyl functionalities, have been used to replace BPA in several applications (Schöpel et al., 2016). In recent years, these chemicals have frequently been detected in surface waters. According to environmental monitoring studies, BPA was still the major bisphenol analogue found in China, the United States, Japan, South Korea, Germany, Italy and other countries (Chen et al., 2016). In 2002, the highest concentration of BPA detected in the Kogawauchi and Kiyotake rivers in Japan was 900 $ng \cdot L^{-1}$ (Kang and Kondo, 2006). As the second most frequently detected analogue, BPF concentrations exceeded 1000 $ng \cdot L^{-1}$ at several study sites in river samples from Japan, Korea and China, reaching up to 2850 $ng \cdot L^{-1}$ in the Tamagawa River in Tokyo (Chen et al., 2016; Yamazaki et al., 2015; Yan et al., 2017). Moreover, BPAF was detected in Taihu Lake, the Liaohe River, the Hunhe River, the Jiaxing Section of Hangzhou Bay and the Xitang River in Jiaxing, China (Jin and Zhu, 2016; Song et al., 2012; Yang et al., 2014), with the maximum concentration in the Xitang River reaching 15,300 $ng \cdot L^{-1}$ in an area around a BPAF manufacturing plant (Song et al., 2012). In view of the high rates of detection and detected concentrations, it is important to determine if the presence of BPA and its analogs in surface waters pose a threat to aquatic ecology.

Water quality criteria is of great importance to management of water environments because they support the establishment of water

* Corresponding author.
E-mail address: yangjx@njnu.edu.cn (J. Yang).

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quality standards and can be used to assess risk levels. Criteria for a number of chemicals have been established by the United States Environment Protection Agency (USEPA) (https://www.epa.gov/wqc) and the Canadian Council of Ministers of the Environment (CCME) (http://ceqg-rcqe.ccme.ca/en/index.html) to protect aquatic life from contaminants. However, these criteria do not cover newly presented pollutants, such as BPA and its analogs.

The species sensitivity distribution (SSD) method, which is currently the most widely used in the development of water quality criteria, reflects the safety threshold of pollutants against most environmental organisms by deducting the concentration of chemicals (HC_5) that harm 5% of species (i.e., it protects 95% of species) (Balk et al., 1995). However, a minimum sample size (number of data) is required to establish a species sensitivity distribution curve. Different guidances are provided by different countries or organizations. For example, the USEPA proposes a minimum of eight endpoints from three phyla and eight classes (U.S. U.S. EPA(US Environmental Protection Agency), 1985), while Australia requires five biotoxicity datapoints for at least four different taxa (ANZECC Australian and New Zealand Environment and Conservation Council, 2000), the Netherlands requires chronic toxicity data from not less than four organisms (RIVM Netherlands National Institute for Public Health and the Environment, 2001), and the Organization for Economic Co-operation and Development (OECD) believes the SSD method can be applied if data are available for five or more species (Balk et al., 1995). As an environmental endocrine disruptor, BPA has been adequately investigated for its aquatic toxicity; however, existing studies of BPF and BPAF have mainly focused on higher mammals such as mice and rats, and aquatic toxicity research is relatively limited. To date, data describing the toxicity of BPF and BPAF against only three aquatic organisms, zebrafish, daphnia, and green alga, have been reported (Ren et al., 2017a, 2017b; Brennan et al., 2006; Tatjana et al., 2016). To derive the water quality criteria of BPF, BPAF and BPA, it is essential to obtain necessary aquatic toxicity data, especially chronic toxicity data pertaining to growth and development.

This study provides supplemental short-term lethality and long-term sublethality toxicity data for BPF and BPAF towards *Chironomus tentans*, *Marisa cornuarietis* and *Scenedesmus obliquus*. Specifically, data from the literature and this study were used to employ the SSD method to determine acute and chronic HC_5 values for BPA, BPF and BPAF, as well as to derive their criteria maximum concentrations (CMCs) and criteria continuous concentrations (CCCs) for aquatic organisms. Finally, the aquatic ecological risk was evaluated by comparing the detected concentrations of BPA, BPF and BPAF in typical rivers to the derived chronic criteria of CCCs.

2. Materials and methods

2.1. Chemicals and test solutions

Bisphenol A ([4,4′-(1-methylethyliden)bisphenol], CAS No.: 80–05-7, purity > 98.0%), bisphenol F ([4,4′-dihydroxydiphenylmethane], CAS No.: 620–92-8, analytically pure), and bisphenol AF (4,4′-(hexafluoroisopropylidene)diphenol, CAS No.: 1478–61-1, purity > 98.0%) were all purchased from TCI (Shanghai) Development Co., Ltd. and used to prepare BPA, BPF and BPAF stock solutions of 10.0 $g{\cdot}L^{-1}$ with acetone.

Before the toxicity test, stock solutions were added to the test container, after which the acetone was allowed to evaporate at room temperature. The test medium (dechlorinated tap water or growth medium) was then added to the container and subjected to ultrasound for 20 min to make it homogeneous. In parallel, a solvent and a blank control group was set up. The concentrations and chemical stabilities were confirmed by chemical analysis.

2.2. Toxicity data collection and screening

Acute and chronic toxicity data for BPA, BPF, and BPA were obtained from the USEPA ecotoxicology database (database ECOTOX, http://www.epa.gov/ecotox/) and relevant literature was acquired from the ScienceDirect search engine (https://www.sciencedirect.com/), the China National Knowledge Internet (http://www.cnki.net/) and government documents. For the acute toxicity data, the median effect concentration (EC_{50}) or median lethal concentration (LC_{50}) was applied as the measurement endpoint. For the chronic toxicity data, the no observed effect concentration (NOEC) or 10% effective concentration (EC_{10}) was applied. To obtain more reproducible toxicity data, only the endpoints of demographic importance at the individual and population level, such as mortality, growth, development and reproduction, were used. Secondary supplemental endpoints such as vitellogenin, other proteins, histology and other biomarkers were ruled out because of their weak ecological relevance. If there were multiple toxicity data for the same species, a geometric mean value was calculated because inclusion of more than one study for a single species in an SSD would introduce bias. When it was not possible to do so, for example when toxicity was based on different test durations, the greater toxicity was selected to ensure the worst case scenario.

The experimental methods for the selected data were consistent with standard methods, such as toxicity test methods published by the OECD, the American Society for Testing and Materials, or China's national standards. For species with no available standard, the methods and results should be described sufficiently. The toxicity results based on the measured concentration were selected with priority. For data based on the nominal concentration, evidence to maintain the test concentration at stable levels during the test period should be provided.

At minimum of five species from at least three taxonomic groups were selected to describe the toxicity to aquatic species. Further acute and chronic toxicity tests were conducted for BPF and BPAF because of their insufficient data size.

2.3. Toxicity test of BPF and BPAF

2.3.1. Test organisms

Chironomus tentans was obtained from the Shanghai Research Institute of Chemical Industry and bred in our lab. *Marisa cornuarietis* was purchased from Nanjing QiQiaoWeng Pet Market and acclimated for 2 weeks. Organisms were acclimated in 10 L glass tanks with dechlorinated tap water (pH 7.5 ± 0.1, water hardness 135 ± 5 mg/L $CaCO_3$) and artificial sediment (peat 5%, kaolin clay 20%, quartz sand 75%; pH 7.3). The tanks were covered with gauze to prevent organisms from escaping. Embryos produced by midges and snails were transferred to new tanks to be cultivated for the test. The conditions were maintained as follows: temperature 23 ± 1 °C; photoperiod (L: D) = 16:8; light intensity 1000 ± 300 lx; mild aeration; feeding daily with a finely ground suspension of fish food.

The green alga *Scenedesmus obliqnus* (FACHB-12, Freshwater Algae Culture Collection at the Institute of Hydrobiology) was maintained in BG11 nutrient solution in a temperature-controlled room (23 ± 1 °C) on an orbital shaker at 120 rpm under continuous fluorescent illumination (5000 ± 500 lx). Algal cells in the exponential phase were used for tests.

2.3.2. Toxicity testing

In the chironomus acute immobilization test, newly hatched first instar larvae (< 24 h post hatching) were exposed to different concentrations of BPF (200, 400, 800, 1600, and 3200 $\mu g{\cdot}L^{-1}$) and BPAF (50, 100, 200, 400, and 800 $\mu g{\cdot}L^{-1}$). Four replicates were exposed to each concentration for each BPA analogue using 20 larvae arising from four different egg masses (same age or days after hatching), and each sample consisted of four replicates (n = 20). Observations were made with a stereomicroscope every 24 h to enumerate the inhibited larvae,