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Screening of high phytotoxicity priority pollutants and their ecological risk assessment in China's surface waters

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HIGHLIGHTS

- Protection of aquatic plants were ignored in risk assessment of pollutants.
- Five high phytotoxicity pollutants were screened from 126 priority pollutants.
- The water quality criteria of the five pollutants were calculated by SSD method.
- Among the five pollutants, DBP and BBP had some risks in water bodies of China.

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ABSTRACT

The protection of aquatic plants has received less attention in ecological risk assessment of pollutants compared with animals. Some pollutants like herbicide, however, are more toxic to aquatic plants than to animals. Aquatic toxicity data of 126 priority pollutants were screened and analyzed in this study. Through data analysis, five priority pollutants namely 1,1,1-trichloroethane (1,1,1-TCA), 4-nitrophenol (4-NP), butylbenzyl phthalate (BBP), di-n-butyl phthalate (DBP) and N-nitrosodimethylamine (NDMA) were identified to have high phytotoxicity effect. The most sensitive aquatic plants to these five pollutants are all alage, including *Chlamydomonas reinhardtii*, *Pseudokirchneriella subcapitata*, *Gymnodinium breve*. The water quality criteria concentration of the five pollutants were derived by the species sensitivity distribution method. The acute criteria concentration for the five pollutants were derived to be 1474, 2180, 54.41, 98.52 and 520.4 $\mu g\ L^{-1}$, and the chronic criteria concentration for them were 147.4, 218.0, 5.441, 9.852 and 52.04 $\mu g\ L^{-1}$, respectively. For China's freshwater bodies, the results of ecological risk assessment based on the derived criteria showed that, for the selected pollutants except DBP, there were basically no significant risk in most of the studied water bodies. DBP showed apparent ecological risks in all of the studied water bodies, particularly in the middle Yellow River, the Xuanwu Lake, the Yuehu Lake, etc. Field monitoring data of the Liao River and the Taihu Lake showed that DBP had moderate risks in some of the sampling sites of both the watersheds, while BBP posed moderate risks only on a few sites of the Liao River.

1. Introduction

Aquatic plants are important components in the aquatic ecosystem (Wang, 1986; Lewis and Pryor, 2013). They produce oxygen and organic substances which most other aquatic lives rely on (Benenati, 1990). Aquatic plants can also function to purify water and provide shelters and habitats for other organisms. Besides, plants are vital to the aquatic nutrient cycling and sediment stabilization (Benenati, 1990; Freemark and Boutin, 1995). So aquatic plants are essential to the normal functioning of the aquatic ecosystem.

Toxicologists generally believed that the sensitivities of the aquatic plants to pollutants were lower than animals (Kenaga and Moolenaar, 1979; Silva et al., 2013). With that assumption, in the hazard assessment of environmental pollutants in aquatic ecosystems, the hazardous effects on aquatic plants have not attracted enough attention, and the toxicity tests for plants have been conducted less frequently than for animals (USEPA, 2001). For example, in OECD Guidelines for the Testing of Chemicals, there are only two toxicity tests methods on aquatic plants out of the total sixteen toxicity tests methods (OECD, 2006, 2011); and only 10% of the results that submitted for the Toxic Substance

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Control Act (TSCA) premanufacturing notification process are for phytotoxicity tests (Lewis, 1995). However, some studies showed that aquatic plants might be more sensitive to pollutants than animals. For instance, previous studies demonstrated that wastewater may have no apparent toxic effects on fish, crustaceans and fleas but can jeopardize or even kill aquatic plants (Berry, 1984; Gericha and Mayesa, 1986). The sensitivities of plants and animals have been compared in some circumstances and found to be chemical- and species-specific (Lewis, 1995), but the toxicity data analysis for a wide spectrum of chemicals are lacking.

Water quality criteria (WQC) lay the scientific foundation of water quality standards (WQSs) (Yan et al., 2013) and play an important role in ambient water environment management. During the deriving process of WQC, only one toxicity data of aquatic plant is required in the US, Canada and other countries, while more toxicity data of animals are needed (Stephen et al., 1985; CCME, 1991; Yan et al., 2013; Wang et al., 2013a). This is probably because that the sensitivities of the aquatic plants to pollutants are assumed to be lower than those of aquatic animals (as mentioned above) or the toxicity test methods for plants and the illumination of the test results were not yet mature (Stephen et al., 1985; Creton et al., 2014). Therefore, the WQC developed based on toxicity data for mainly aquatic animals may not be effective to protect aquatic plants (Blaylock et al., 1985).

The ecotoxicity data used in ecological risk assessment of priority pollutants were mostly animals' data, and it is not clear that which pollutants are more toxic to plants than to animals. Given the importance of plants in aquatic ecosystem and the uncertainty of their sensitivities, aquatic plants and the pollutants with high phytotoxicity should be screened systematically to provide references for aquatic ecosystem risk assessment. In this study, pollutants with high phytotoxicity were screened from 126 priority pollutants defined by the U.S. Environmental Protection Agency USEPA (2014), and the WQC of the screened pollutants were derived to evaluate their ecological risks in China's surface water bodies, including the Liao River and the Taihu Lake.

2. Materials and methods

2.1. Screening of high phytotoxicity priority pollutants

The 126 priority pollutants of the USEPA (2014) were chosen as the target pollutants in the present study. Toxicity data of these pollutants were collected and screened according to the US guidelines for deriving WQC (Gericha and Mayesa, 1986).

The ecotoxicity data for the 126 priority pollutants were collected from the ECOTOX database (http://cfpub.epa.gov/ecotox/), TOXLINE database (http://toxnet.nlm.nih.gov/) and published literatures. Data originated from the tests with unsuitable exposure time, unqualified dilution water (such as pure water), unscientific experimental design (such as no control group) and relatively insensitive life stages were excluded during the screening process. As for the acute test endpoints of aquatic animals, the 48 h-LC_{50} or EC_{50} for daphnia or midge larvae, and 96 h-LC_{50} or EC_{50} for fish, mollusks, shrimp and other organisms were chosen (Wang et al., 2013b). For the aquatic plant, according to the guidelines of the US (Stephen et al., 1985), toxicity data from the tests with all endpoints and parameters can be used in the development of WQC because the methodologies of plant's toxicity test are not mature. Moreover, the acute and chronic toxicity data for plants were not discriminated as long as the exposure time was not shorter than that of animals (i.e., not less than two days). The effect parameters of the plant's toxicity test include EC_x (x% effective concentration), no observed effect concentration (NOEC), lowest observed effect concentration (LOEC) and so on, and the endpoints include reduction in cell count or growth, cell division inhibition, lethal dose, reduced chlorophyll, etc.

For one species, when more than one toxicity data were available, geometric mean values of the toxicity data were used for calculation, known as species mean values (SMVs) (Stephen et al., 1985). The species were ranked based on their SMVs values (from the lowest to the highest). The lower the rank is, the more sensitive the species is. Then the sensitivity distribution of the aquatic organisms to these screened priority pollutants with high phytotoxicity were generated. The priority pollutants are considered to have high phytotoxicity when plant is ranked to be the first.

2.2. Development of WQC for the high phytotoxicity priority pollutants

The species sensitivity distribution (SSD) method was employed to derive the WQC of the high phytotoxicity priority pollutants (Yan et al., 2012). The median HC_5 (hazardous concentration at which 5% of the species are potentially affected) and the 90% confidence interval of the normal distribution was calculated using the program ETX 2.0 (Van Vlaardingen et al., 2004). The program is based on the method developed by Aldenberg et al. (2000), which is recommended by the National Institute for Public Health and the Environment (RIVM) of the Netherlands (Van Vlaardingen and Verbruggen, 2007).

The derivation method of the acute WQC is as follows:

$$\text{Acute WQC} = HC_{5,\text{acute}}/AF \quad (1)$$

where AF is an assessment factor between 5 and 1, reflecting the further uncertainties identified. The AF is determined to be 2 in most studies (Stephen et al., 1985; Van Sprang et al., 2004).

There are different approaches to derive chronic WQC for different quantity of chronic data. If the chronic toxicity data are sufficient to build the SSD curve, the chronic HC_5 can be derived by SSD method, and then the chronic WQC could be obtained (Eq. (2)).

$$\text{chronic WQC} = HC_{5,\text{chronic}}/AF \quad (2)$$

However, chronic toxicity data is often deficient due to high cost and prolonged time required to perform such studies. An alternative approach is using the acute to chronic ratio (ACR) to extrapolate the continuous criteria concentration (CCC) (Eq. (3)) (Chen, 2005; Wang et al., 2009).

$$\text{chronic WQC} = HC_{5,\text{acute}}/(ACR \times AF) \quad (3)$$

The data used to calculate the ACR should come from at least three species: one fish, one invertebrate and one acutely sensitive organism, of which both acute and chronic toxicity experiments were conducted in the same laboratory (Stephen et al., 1985). If a qualified ACR cannot be calculated, a default value of 10 was recommended by USEPA (1986) and OECD (1992). In this study, the AF was determined to be 2 according to the guidelines of the US (Stephen et al., 1985).

2.3. Field monitoring in the Liao River and the Taihu Lake

One liter of water sample was collected in September 2012 from every sampling site in the Liao River (located in northeast China) and the Taihu Lake (located in eastern China) and stored in brown glass bottles. There are a total of 25 sampling sites in the Liao River and 37 sampling sites in the Taihu Lake (Figs. 3 and 4). All samples were refrigerated at 4 °C before extraction and analysis. The samples were filtered through 0.45 μm glass-fiber membrane, and the filtered water samples passed through activating solid phase extraction (SPE) cartridges at a flow rate of 10 mL min^{-1}. The cartridges were then eluted with a 5 mL ethyl acetate followed by a 5 mL methylene chloride and 3 mL ethyl acetate/methylene chloride (1:1 v/v) (USEPA, 1995; MWRPRC, 2007). The eluants were