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Water quality criteria derivation and ecological risk assessment for triphenyltin in China

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ABSTRACT

Triphenyltin (TPT) is one of the most toxic chemicals artificially discharged into aquatic environment with human activities. Due to its intensive use in antifouling paints and adverse effects on non-target species, TPT has aroused wide concern in both saltwater and freshwater environment. Nevertheless, the water quality criteria (WQC) are not available in China, which impedes the risk assessment for this emerging pollutant. This study aims to establish the WQC of TPT for both freshwater and saltwater ecosystems. With the derived WQC, a four-level tiered ecological risk assessment (ERA) approach was employed to assess the ecological risks of this emerging pollutant in Chinese waters. Through the species sensitivity distribution (SSD) methodology, the freshwater criterion maximum concentration (CMC) and criterion continuous concentration (CCC) were derived as 396 ng Sn L^{-1} and 5.60 ng Sn L^{-1}, respectively, whereas the saltwater CMC and CCC were 66.5 ng Sn L^{-1} and 4.11 ng Sn L^{-1}, respectively. The ecological risk assessment for TPT demonstrated that the acute risk was negligible whereas the chronic risk was significant with HQ (Hazard Quotient) values of up to 5.669 and 57.1% of coastal waters in China facing clear risk. TPT contamination in coastal environment, therefore, warrants further concern.

1. Introduction

Triphenyltin (TPT) compounds are triphenyl derivatives of tetravalent tin with a general formula of $(C_6H_5)_3$Sn-X, typically existing as chloride, hydroxide and acetate compounds (Yi et al., 2012). TPT, together with TBT (tributyltin), has been widely applied in antifouling paints and fungicides since 1960s. In European countries and USA, TBT was the main ingredient in organotin based antifouling paints. In China, however, TPT was the mainly used organotin product with an annual manufacturing amount of 150–200 t (Hu et al., 2006; 2009). Due to its properties of persistence, bioaccumulation and toxicity, TPT has received wide concern. TPT exerts endocrine disrupting effects on various aquatic species including gastropods and fishes (Horiguchi et al., 1994; Santos et al., 2006; Zhang et al., 2008; Sun et al., 2011), causing reproductive failure and population decrease at extremely low concentrations of nanogram per liter. Consequently, the usage of organotin-based antifouling paints was prohibited in many countries and regions throughout the world (Chau et al., 1997). The international ban for organotins was also initiated by IMO (International Maritime Organization) in 2001 (IMO, 2001). In China, although TBT is regulated, TPT is not restricted except for its usage as pesticides being prohibited in 1999 in Taiwan (Meng et al., 2009). Due to the increasing demand for its usage in both industrial and agricultural sectors in China, TPT contamination in natural waters is to be expected (Cao et al., 2009). TPT in coastal waters of China was reported with concentrations from undetected to 17.2 ng Sn^{-1} (Wang et al., 2008, Liu et al., 2011, Hu et al., 2006, Huang, 1999). TPT was also reported in fresh water in the Yangtze River and Jialing River with a concentration of up to 37.2 ng Sn^{-1} (Gao et al., 2013).

Water quality criteria (WQC) are defined as the permitted maximum concentration of chemicals without negative effects on organisms in aquatic environment (Yang et al., 2014). The two-number criteria system, including criterion continuous concentration (CCC) and criterion maximum concentration (CMC) is most commonly used in various countries, which is also adopted in this study. The combination of CMC and CCC provides an appropriate extent of protection for aquatic organisms from both acute and chronic toxicity (USEPA, 1985).

According to the guidelines of US EPA, the ecological risk assessment (ERA) is aimed to determine the probability and degree of harmful ecological outcome of risk sources such as chemical exposure (USEPA, 1998). The most rudimentary approach of ERA is hazard quotients (HQ), usually expressed as a ratio between exposure and

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toxicity concentrations. Despite its simplicity and effectiveness, the quotients do not allow spatial or temporal analysis of the probability and magnitude of ecological risks (ECOFRAM, 1999). To obtain more reliable estimates of risks, ERA based on probabilistic analysis, which quantifies the risk through probability distributions of both exposure and effect, are recommended for higher level assessment (Solomon and Sibley, 2002).

This study aims to develop the WQC of TPT considering both exposure duration (acute and chronic) and water types (saltwater and freshwater). Based on the WQC, the ecological risk of TPT in aquatic environment of China were comprehensively evaluated with a tiered ERA approach.

2. Materials and methods

2.1. Screening of toxicity data

The toxicity data of TPT were screened from open databases and literature in this study. Only the toxicity data tested with Chinese resident species were selected. For acute toxicity data, short-term (48 h or 96 h) LC_{50} or EC_{50} (median lethal or effective concentration) values were adopted. While for chronic data, long-term (≥ 14 days) NOEC (no observed effect concentration) values referring to traditional toxicity endpoints such as survival and growth were used. The toxicity data referring to molecular biomarker endpoints were however excluded. The geometric mean was employed when multiple data was available tested with the same species (Guo et al., 2015). The toxicity values of TPT selected for criteria derivation in this study is listed in Supplementary Material S1–S2.

2.2. The derivation of water quality criteria

Nowadays, the SSD (species sensitivity distribution) methodology is increasingly adopted in water quality criteria derivation (Wik, 2008). This methodology is based on the hypothesis that the tested species are representative, in terms of sensitivity, of the total species in an ecosystem (Ciffroy and Brebbia, 2007). SSD is used to predict Hazardous Concentration affecting p% of all species in an ecosystem (HCp), usually selecting 5% as the acceptable fraction affected and therefore 95% species being protected. Based on the value of HC_5 derived with the SSD model, the Predicted No Effect Concentration (PNEC) could be determined through being divided by an Assessment Factor (AF). The choice of AF depends on the richness of toxicity data and the goodness of model simulation (ECB, 2003; Gao et al., 2014). Currently an AF of 2 is used in most studies when the toxicity data covers at least three phylum and eight families (USEPA, 1985; Guo et al., 2015; Park et al., 2018). The same AF value was also applied in the criterion derivation process in this study to ensure the consistency of results.

Although various distributions have been utilized to construct SSD models, the log-normal distribution is most commonly used with its advantage of in depth analysis for various uncertainties, which is also adopted in this study for SSD construction.

2.3. Ecological risk assessment

The risk assessment of TPT was conducted based on a four-level tiered ERA approach recommended by ECOFRAM (1999) and developed by Zolezzi et al. (2005) and Wang et al. (2009). The assessment approach is as follows:

Level 1 assessment involves a deterministic hazard quotient (HQ), *i.e.,* a ratio between MEC (measured environmental concentration) and PNEC values. The PNEC was referred to the derived criteria of TPT. The risk level is determined as negligible, potential and clear based on HQ values with the corresponding range of 0–0.3, 0.3–1.0 and over 1.0, respectively.

Level 2 assessment calculates the likelihood that the measured concentrations exceed the preselected effect threshold by comparing the exposure concentration distribution (ECD) with the WQC. The log-normal model was adopted for constructing ECD after Kolmogorov-Smirnov test for normality.

Level 3 assessment characterizes the risk through the overlap between SSD and ECD. Firstly, MOS_{10} (Margin of Safety at 10%) was quantified via the 10th percentile of SSD (SSD_{10}) divided by the 90th percentile of ECD (ECD_{90}). MOS_{10} values of < 1 indicate significant risk, whereas values of > 1 represent minimal risk to aquatic organisms. The MOS_{10} method therefore only provides general information of risk. To further characterize the risk, the Joint Probability Curve (JPC) generated from SSD and Exceedance Probability Function (EPF, or the reverse ECD) represents the probability of exceeding the pollutant concentration causing a certain degree of ecological effect (Wang et al., 2002). Based on JPC, the Overall Risk Probability (ORP) can be calculated as the area of JPC enclosed by the X-axis to identify the overall ecological risk. The risk level is ranked as negligible, potential and clear if the ORP value is < 0.1%, 0.1–1.0% and ≥ 1.0%, respectively (Wang et al., 2009).

Level 4 assessment adopts Monte Carlo random sampling from ECD and SSD for 20,000 times and consequently calculates the distribution-based quotient (DBQ). The risk is expressed as the likelihood of exceeding the preselected HQ values (0.3 or 1.0).

3. Results and discussion

3.1. Acute and chronic toxicity data of TPT

Table 1 presents the statistical parameters for acute and chronic datasets of TPT to both freshwater and saltwater species. The Anderson-Darling test showed that the toxicity data could be fit with log-normal distribution. A two-sample *t* test indicated that both acute and chronic data showed significant difference between freshwater and saltwater ($P_{acute} < 0.01$, $P_{chronic} < 0.05$). It is, therefore, necessary to derive saltwater and freshwater criteria separately to avoid over or under protection of aquatic species.

3.2. Acute WQC for TPT

The SSD models were constructed based on the acute data of TPT to saltwater and freshwater species, respectively (Fig. 1a). The HC_5 (hazardous concentration to 5% of species) values were calculated as 0.133 μg Sn L^{-1} (90% confidence interval: 0.039–0.290 μg Sn L^{-1}) and 0.791 μg Sn L^{-1} (90% confidence interval: 0.273–1.652 μg Sn L^{-1}) respectively for saltwater and freshwater species. With the HC_5 values, the PNEC values could be calculated by being divided with an AF of 2, which is also defined as WQC for TPT. Consequently, the CMC (criterion maximum concentration) in saltwater and freshwater was derived as 0.067 μg Sn L^{-1} and 0.396 μg Sn L^{-1}, respectively.

3.3. Chronic water quality criteria of TPT

Considering the scarcity of chronic toxicity data, the method of Acute to Chronic Ratio (ACR) was used to supplement saltwater chronic data. A final ACR value of 18.1 was adopted as the geometric mean of all ACR values (Supplementary Material S3). During the simulation of SSD curves for saltwater species, both the raw data and ACR extrapolated data were pooled (Supplementary Material S4). During the simulation of SSD curves for freshwater species, however, only the raw data was used since they were sufficient for model simulation. Based on SSD simulation, the HC_5 values for saltwater and freshwater species were quantified as 0.0082 μg Sn L^{-1} and 0.011 μg Sn L^{-1}, respectively (Fig. 1b). Consequently, the CCC (criterion continuous concentration) was derived as 0.0041 μg Sn L^{-1} and 0.0056 μg Sn L^{-1} for saltwater and freshwater environment.