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pH-dependent ecological risk assessment of pentachlorophenol in Taihu Lake and Liaohe River

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ABSTRACT

Pentachlorophenol (PCP) has been reported toxic to aquatic organisms, and it frequently occurs at relatively high concentrations in most Chinese waters due to the re-emergence of schistosomiasis since 2003. Several studies about Water Quality Criteria (WQC) for PCP had been performed to protect the aquatic ecosystem, but in most of these studies the toxicity data were not properly analyzed (e.g. screening and processing methods). Moreover, little study was carried out on the ecological risk assessment (ERA) based on environmental factors. In this study, through collecting published native toxicity data of PCP along with relationships between toxicity and pH, pH-dependent WQC was established using a standardized scientific statistical method in China. The Criterion Maximum Concentration (CMC) and Criterion Continuous Concentration (CCC) were expressed as a function of pH. These were (1) CMC = exp(1.361 × pH-8.034) and (2) CCC = exp(1.361 × pH-10.434). At pH 7.8, the derived CMC and CCC were 13.21 and 1.20 μg/L, respectively. In addition, four tiers of the ERA were conducted based on pH for different waterbodies at different seasons. In tiered 1, 2, 3 and 4 ERA, PCP exposure concentrations were standardized to that at pH 7.8. Results showed that all levels of ERA method in the tiered framework were consistent with each other, and the risks of PCP in Liaohe river of wet season, Taihu lake and Liaohe river of dry season increased successively. The Hazard quotient (HQ) method indicated that small fluctuations in pH would lead to misleading hazard results. PCP concentrations of 8.66 μg/L at pH 7.37 in one site posed more risk than PCP of 9.57 μg/L at pH 7.93 in another site. The joint probability suggested that ecological risks may exist 11.84% in the dry season and 1.51% in the wet season in Liaohe River, and 4.98% in Taihu Lake, respectively while 5% thresholds (HC_5) were set up to protect aquatic organisms. We hope this work could provide more information to manage and control PCP pollution in Taihe Lake and Liaohe River.

1. Introduction

Pentachlorophenol (PCP) is one of the agrochemicals, that has been extensively used as fungicide, wood preservative, herbicides and insecticides since the 1930s in China and other countries (Cheng et al., 2015; Ge et al., 2007; Geyer et al., 1987; Heudorf et al., 2000). As a persistent organic pollutant (POP), an endocrine disrupting chemical (EDC) (Zha et al., 2006) as well as a class 2B carcinogen (Ge et al., 2007), PCP has been listed as one of the priority pollutants in aquatic environment in both the USA and China (Jin et al., 2012; USEPA, 1991; Xia and Zhang, 1990). Although PCP was restricted to be produced and used in China in 1997 due to its potential ecological risk, the production and use of PCP for schistosomiasis control and snail elimination has increased once again because of the re-emergence of schistosomiasis in the east of China (Yang et al., 2012). Only in 2003, the PCP production reached about 3000 t (Tan and Zhang, 2008). Due to its wide usage, high concentrations of PCP have been detected in most surface waters in China (Jin et al., 2012; Zhong et al., 2010). Recently, a great number of studies on toxicity of PCP have been conducted (Fisher et al., 1999; Saarikoski and Viluksela, 1981; USEPA, 1986; Xing et al., 2012a). The results of these studies have proved that differences in pH can affect the toxicity of PCP greatly. For example, the toxicity of PCP at pH 6.0 to *Daphnia magna* is 45.71 times higher than that at pH 9.0 (Yu et al., 1997). This is because the PCP molecule is much

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more toxic than its ionic form, and pH alters the relative proportion of molecules to ions in waterbodies (Arcand et al., 1995; Blum and Speece, 1990; Xing et al., 2012a).

Recently, there have been increasing studies aimed at deriving water quality criteria (WQC) and assessing ecological risks of environmental pollutants in China (Wang et al., 2013; Wu et al., 2015; Xing et al., 2012a; Yan et al., 2012). With the in-depth study of WQC, many researchers found that the toxicity of some metals (e.g. copper and cadmium) (USEPA, 2007, 2016), few inorganic and organic toxicants (e.g. ammonia and PCP) (USEPA, 1986, 2013) was significantly influenced by physical-chemical characteristics (e.g. hardness, temperature, pH and etc.) of waterbodies. Consequently, it is more appropriate to derive WQC considering water quality factors for certain pollutants. As for PCP, because of the influence of pH on PCP toxicity, it is necessary to estimate WQC thresholds based on toxicity data at different pH values (USEPA, 1986). WQC had been derived dependent on pH by Xing et al. (2012a, 2012b), but more efforts could be put into the selection of toxicity data and the methodology to be more accurate such as the standardization of toxicity data.

Different environmental risk assessment (ERA) methods have been developed to assess environmental risks of chemicals (Wang et al., 2009). Among these methods, hazardous quotient (HQ) method is the most commonly used because of its simplicity (Wu et al., 2015). However, HQ is a single-point evaluation method which is only suitable for conservative risk assessment at screening level. To evaluate the environmental risk of chemicals, probabilistic assessments are used in order to quantify the likelihood of toxic effects occurring. This can be done by combining the distribution of exposure concentrations of a chemical and toxicity to multiple species (i.e. Joint Probability Curve) (Hunt et al., 2010; Solomon et al., 2013; Wang et al., 2012). In order to get more reliable ERA results, a number of studies have proposed a tiered approach (i.e., both deterministic method and probabilistic method) to characterize environmental risks of chemicals (Jin et al., 2012; Wang et al., 2009; Zolezzi et al., 2005). Though there have been studies on ecological risks of PCP in China in recent years, none of them took into account the influence of pH on the toxicity of PCP (Jin et al., 2012; Xing et al., 2012b; Zhong et al., 2010). Hence, it is rational to evaluate the ecological risks of PCP based on the pH of waterbodies.

In China, Taihu Lake near Shanghai City is one of the five largest fresh water lakes (Zhong et al., 2010), and Liaohe River located in Liaoning and Jilin province (Northwest China) is one of the seven major rivers (Yang et al., 2011). They are surrounded by agricultural land and industrial areas, and constitute the main sources of drinking water supplying lots of cities and villages (Kong et al., 1998). However, with the development of agriculture and industry, more and more pollutants containing PCP were released into Taihu Lake and Liaohe River directly or indirectly (Tan et al., 2009; Zhong et al., 2010). The ecology of these two aquatic systems has been deteriorating as a result.

In this study, WQC of PCP based on different pH values was derived using a statistical method based on the toxicity data from native aquatic organisms. In addition, after standardization of PCP exposure concentrations to that at a certain pH, a tiered ERA for PCP was conducted in both the Taihu Lake and the Liaohe River.

2. Materials and methods

2.1. Environmental concentrations

2.1.1. Sample collection and analysis

A total of 31, 31 and 37 surface water samples from the Liaohe River during the wet season (July) and dry season (November) and the Taihu Lake (July) in the year of 2014 were collected, respectively (Fig. 1). The locations of sampling sites were recorded in situ using a global positioning system (GPS). Grab water samples were taken at 1 m depth with pre-cleaned stainless steel bucket, and then filtrated through 0.70 μm glass filter membrane. The filtered water samples were stored in 1-L glass amber. Water samples were transported to the laboratory on ice and stored at 4 °C in the darkness until further analysis. The pH values of water samples in all sampling sites were determined in situ using a portable pH meter (HACH, HQ40d).

2.1.2. Chemicals analysis and quality control

The filtrated water samples were extracted using a solid-phase extraction (SPE) system following the method in the previous study and report with slight modifications (Gao et al., 2008; Zhou et al., 2000). Briefly, reversed phase C18 cartridges (Supelclean ENVI-18) were used to adsorb PCP. After extraction, the cartridges were eluted with 10 mL of methyl alcohol. Then the extract was concentrated to about 0.7–0.8 mL, and the residual water was removed by adding anhydrous sodium sulfate. Then the extract was concentrated to 1 mL and subjected to analysis using gas chromatograph equipped with mass spectrometer (Agilent 7890A and 5975C, USA) in a selected ion mode.

All chemical analyses were strictly conducted following the quality assurance and quality control procedures (Gao et al., 2008; Ge et al., 2007; Ostroukhova and Zenkevich, 2006). PCP was

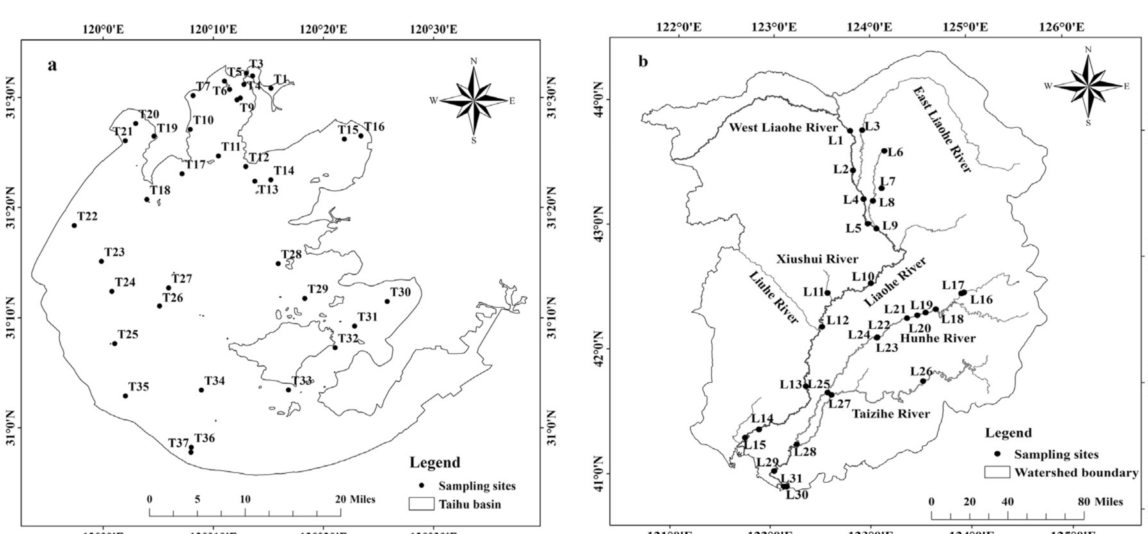

Fig. 1. Sampling sites in Taihu Lake (Fig. 1a) and Liaohe River (Fig. 1b), China.

quantitatively determined using retention time and peak area with references to a calibrated standard curve. Five different concentrations of PCP standards were adopted to establish a calibration curve (linear regression curve with $r^2 \geq 0.99$). Method detection limit (MDL) of PCP, which was 0.18 ng/L, was determined as three times the standard deviation of the baseline noise. Average recoveries of PCP in water samples were in the range of 92.7–116%.

2.2. Effect assessment

2.2.1. Toxicity data collection and selection

Toxicity data of native species for PCP and the corresponding pH values were collected and selected from the ECOTOX database (http://cfpub.epa.gov/ecotox/), China Knowledge Resource Integrated Database (http://www.cnki.net/), PubMed and Web of Science databases. The key words included pentachlorophenol, PCP, China, both separately and combined with risk assessment, water quality criteria, criterion maximum concentration, criterion continuous concentration, environmental exposure, detection, toxicity, concentration and Taihu Lake, Liaohe River. The government documents, research reports and other available data were also captured from literature retrieval. Totally acute data from forty-one species of eight taxonomic groups (Table S1) and chronic data from twenty species of five taxonomic groups (Table S2) were selected respectively. These data were used to describe the effect of PCP on aquatic organisms in surface waters in China.

As for acute toxicity data of PCP, median effect concentration (EC_{50}) was used as the measurement endpoint. If the EC_{50} was not able to be obtained, the median lethal concentration (LC_{50}) was used instead. As for chronic toxicity data, no observed effect concentration (NOEC) was the first choice, but maximum acceptable toxicant concentration (MATC), lowest observed effect concentration (LOEC) or 10% effective concentration (EC_{10}) were used when NOEC was not available. Geometric mean was applied if there were multiple toxicity data for one species (Stephen et al., 1985).

2.2.2. Standardization of toxicity data and environmental concentrations

As suggested by USEPA in the PCP criteria document (USEPA, 1986), toxic concentrations of PCP in different pH values should be standardized to minimize the uncertainty of derived WQC, and the principles of standardization are listed as follows.

1. Normalization of acute toxicity value: calculating the geometric mean of each species' acute values, and then each acute value is divided by the geometric mean of each species. This statistical approach normalizes the acute values, in order that the geometric mean of the normalized values for each species is 1.0.

2. Normalization of pH: calculating the geometric mean of each species' pH values, and then each pH value is divided by the geometric mean of each species. Similarly, the geometric mean of the normalized pH for each species is 1.0.

3. A least square regression is carried out between all normalized acute toxicity values and pH values, and the slope of the linear regression is obtained. The best fitting line will go through this point of (1,1) in the graph.

4. The Species Mean Acute Value of each species was individually calculated according to the following equation:

$$\text{Species Mean Acute Value} = \exp\left(\ln W - V\left(\ln X - \ln Z\right)\right) \tag{1}$$

where W is the geometric mean of each species' acute values, V is the slope, X is the geometric mean of pH for each species, and Z is the value of pH at a selected condition.

In addition, we use the above slope V directly as the slope of standardized exposure concentration, the equation is:

$$\text{Standardized exposure concentration} = \exp\left(\ln A - V\left(\ln B - \ln Z\right)\right) \tag{2}$$

where A is the original exposure concentration at a specific sampling site, V is the slope, B is the original pH at the sampling site, and Z is the value of pH at a selected condition.

2.2.3. Derivation of WQC thresholds

The species sensitivity distributions (SSDs) were established to describe the relationship between each species' toxicity values and their cumulative frequencies (Aldenberg and Slob, 1993; Posthuma et al., 2002; Wheeler et al., 2002). The PCP toxicity data used to construct SSD are shown in the Table S1 and Table S2. In this study, one sample Kolmogorov–Smirnov test was used to check whether log-transformed toxicity values and data of field concentrations conformed to normal distribution using SPSS 18.0. The results revealed that all data fitted the log-normal distribution.

The HC_5 (5% hazard concentrations at which 5% of the aquatic organisms could be affected) is derived from the SSD curve. In this research, forty-one acute and twenty chronic PCP toxicity data were applied to construct acute and chronic SSDs by using a log-logistic distribution model, respectively (Dyer et al., 2008). The Criterion Maximum Concentration (CMC) and Criterion Continuous Concentration (CCC) were calculated respective as the derived HC_5 divided by a factor of 2 (with a 50% uncertainty) (ECB, 2003).

2.2.4. Tiered risk assessment of PCP

A four-level tiered approach was used to assess the PCP risk in this study (Suter, 2008; Wang et al., 2009; Zolezzi et al., 2005).

In Tier1, the HQ method was calculated using only the CCC as toxicity threshold by the following equation:

$$HQ = (\text{Exposure Concentration})/CCC \tag{3}$$

The hypothesis of this method is that potential hazard is likely to occur at any moment if exposure concentration of a pollutant is greater than its CCC. Otherwise, the least possible hazard is anticipated. The four categories of risk are listed below (Wu et al., 2015):

$HQ < 0.1$, there is no risk;
$0.1 \leq HQ < 1.0$, the risk is low;
$1.0 \leq HQ < 10$, the risk is moderate;
$HQ > 10$, the risk is high.

In tiered 2, we used a quantitative probabilistic risk method which compares exposure concentration distributions with toxicity data. Then the probability that the exposure concentration exceeds CCC was calculated. Generally, Kolmogorov–Smirnov test should be used to assess the normal distribution of the exposure concentrations.

In Tier 3, another probabilistic risk method was used. In this case, both exposure and toxicity data distributions were compared, and a margin of safety (MOS_{10}) was calculated as the following equation:

$$MOS_{10} = SSD_{10}/C_{90} \tag{4}$$

where SSD_{10} is the concentration at which 10% of aquatic organisms are out of protection, C_{90} is the 90th percentile concentration for the exposure distribution, and all toxicity and exposure data are log-transformed (Solomon, 1996). In general, MOS_{10} smaller than 1 indicates that distributions of toxicity data and exposure concentration have high coincidence degree and can lead to a high risk to aquatic organisms. MOS_{10} which is greater than one shows that little environmental risk will be posed to aquatic organisms.

Tiered 4 is a joint probability curve (JPC) method which is developed on the basis of Tiered 3 method. Exceedance probability function is made by transforming the exposure concentration distribution, and combined with SSD to generate a JPC. JPC describes the relationship between the probability that aquatic organisms would be affected (X axis) and the exceeded frequency of exposure concentrations (Y axis) (Solomon et al., 2000; Wang et al., 2009; Zolezzi et al., 2005). Each data point on JPC represents both the probability that the proportion of species will be affected, and the frequency in which the magnitude of exposure concentration would be exceeded. The closer JPC is to the X axis, the probability of adverse effects is smaller (Jin et al., 2013; Solomon et al., 2000).

3. Results and discussion

3.1. Derivation of WQC thresholds for PCP

3.1.1. Correlations between pH values and PCP toxicity

In this study, we attempted to find the statistically significant correlations between acute or chronic PCP toxicity and specific pH values.

First, acute PCP toxicity data and pH values were all standardized, and then toxicity data were ln-transformed ($\ln(EC_{50}$ or $LC_{50})$). A linear regression analysis was carried out subsequently between $\ln(EC_{50}$ or $LC_{50})$ and pH values. In the linear regression analysis, the toxicity values including fish, crustaceans, and algae were available for PCP over a pH range (Fig. 2).

The equation is described below.

$$\ln(EC_{50}\text{or } LC_{50}) = 1.361 \times \text{pH} + 4 \times 10^{-17}(\text{Fig.2a, n} = 14,\ r^2 = 0.89,\ p < 0.01) \quad (5)$$

$$\ln(EC_{50}\text{or } LC_{50}) = 0.442 \times \text{pH} - 0.782\ (\text{Fig. 2b},\ n = 14,\ r^2 = 0.63,\ p < 0.01) \quad (6)$$

Parameters have some differences between Eqs. (5) and (6) although the same four species' toxicity data were used. The relative coefficient of r^2 in Eq. (5) is more close to 1 than that in Eq. (6), which indicated that the standardization of both toxicity data and pH was a more accurate mathematical statistic method to reduce the uncertainty in dealing with data, rather than the direct use of pH and ln-transformed toxicity data.

However, the available chronic toxicity data of PCP for one native aquatic species (*Scenedesmus obliquus*) at different pH values are quite poor, thus the relationship between chronic PCP toxicity data and pH values was not able to be constructed. In this case, similar as those studies conducted by USEPA (USEPA, 1986) and other researchers (Chèvre et al., 2006; Xing et al., 2012a), the slope of the acute PCP toxicity against pH was directly applied as the slope of chronic toxicity.

3.1.2. Water quality criteria thresholds for PCP depending on pH

Toxicity data of PCP at different pH values were normalized for pH 7.8, and then CMC and CCC were estimated through SSD analysis on the basis of log-logistic model (Dyer et al., 2008) (Fig. 3). HC_5s were 26.42 and 2.40 μg/L after pH normalization for the acute and chronic exposure, respectively. The estimated CMC and CCC were 13.21 and 1.20 μg/L, respectively (ECB, 2003; Stephen et al., 1985).

Using a linear dependence (Eq. (5)), the final CMC and CCC were expressed as functions of pH (Eqs. (7) and (8)):

$$\text{CMC} = \exp(1.361 \times \text{pH} - 8.034) \quad (7)$$

$$\text{CCC} = \exp(1.361 \times \text{pH} - 10.434) \quad (8)$$

The relationship between CMC or CCC of PCP and pH were compared with other that in other studies (USEPA, 1986; Xing et al., 2012a) (Fig. 4). Generally, the CMC and CCC values derived in this study were lower than that of USEPA over the same pH range. Compared with the CMC- or CCC-pH relationships studied by Xing et al. (2012) (Fig. 4), the CMC value in this study was lower when pH was below 7.5 and higher when pH was above 7.5; the CCC value was lower when pH was less than 9.8 and higher when pH exceeded 9.8. The differences in CMC- or CCC-pH relationships in these studies were attributed to differences in species selection and data processing progress (i.e. standardization of toxicity data). In Xing's study, data from non-native species such as *Rana catesbeiana*, *Pomacea canaliculata*, *Dreissena polymorpha*, *Oncorhynchus mykiss*, *Pimephales promelas* and *Ictalurus punctatus* were used, while in this study, only the data from native species were adopted in the analysis. To date, it is still under debate whether non-native and native species can be pooled together to derive the CMC and CCC as the different sensitivity among species from different regions of the world (specifically temperate vs tropical)

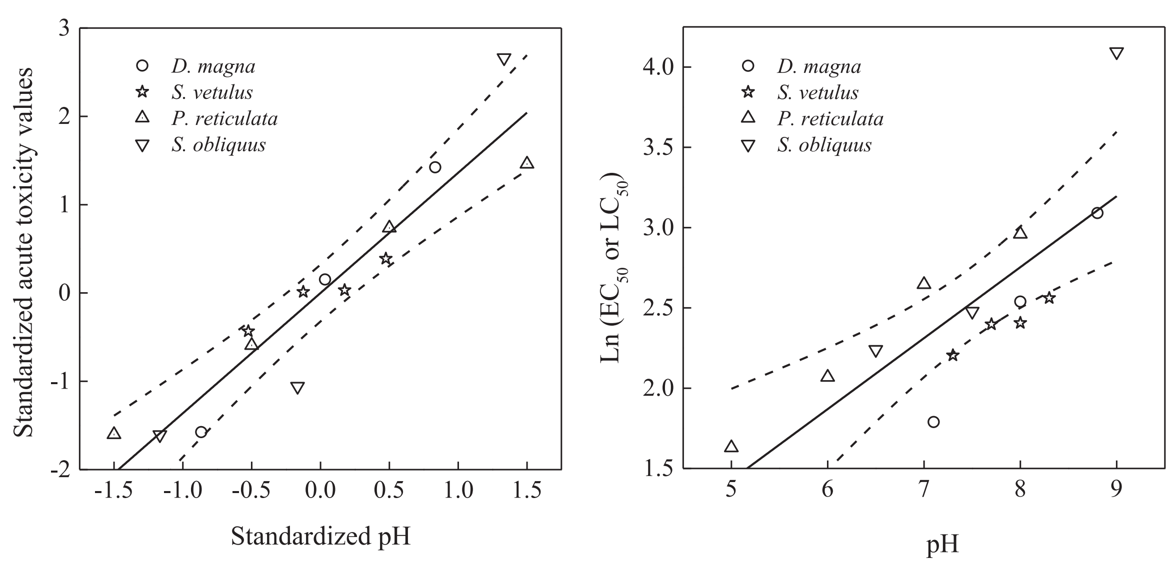

Fig. 2. Relationships between toxicity data and pH. Fig. 2a represents the relationship between standardized acute toxicity data and standardized pH; Fig. 2b described the correlation between ln-transformed acute toxicity data and pH.

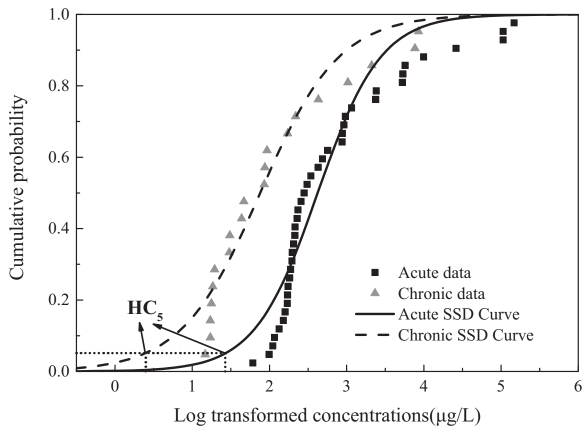

Fig. 3. Two species sensitivity distributions (SSD) for PCP based on acute toxicity (squares and solid line) and chronic toxicity (triangles and stippled line). HC5: concentration affecting 5% of aquatic organisms.

(Kwok et al., 2007; Maltby et al., 2005). Guidelines of US EPA, Australia and New Zealand recommend using toxicity data from only native species to derive WQC to reduce the uncertainty (ANZECC, 2000; Stephen et al., 1985), and the authors of this article agree with this opinion. Therefore, only the toxicity data that collected from species widespread in freshwater in China were taken into account in this study.

3.2. Ecological risk assessment of PCP

3.2.1. Tiered 1 assessment

The explicit HQs of PCP in the Liaohe River (both wet season and dry season) and the Taihu Lake were shown in Table 1. Among all sampling sites, the HQ at L27 of the dry season was the highest (HQ > 10), which indicated a high risk of PCP at this site. The risks of ten sampling sites exhibited in italic in Table 1 were moderate. Low hazards were expected in most water bodies as reflected by their low HQs.

Though the concentration of PCP at T29 was higher than that at L27 of dry season, HQ at T29 (HQ = 6.65) was only about half of that at L27 of dry season (HQ = 12.92). Similarly, though concentrations of PCP at T31 and L12 of dry season were higher than that at L26 of wet season, the risks at these two sites were lower than that at site L26. In addition, though the concentration of PCP at T31 was three times as high as that of L10 of wet season, but the HQ at these two sites were almost the same (HQ was about 0.6). Similarly, HQs at T1 and L25 of wet season were very close to each other, but the PCP concentration at T1 was nine times as high as that at L25. The overall results of HQs and PCP concentrations revealed that the risk levels of PCP in Taihu Lake and Liaohe River were about the same though the PCP concentrations in Taihu Lake were higher (Table 1 and Fig. S1). These were attributed to differences in both the pHs at different sampling sites and the derived CCC values at different pH values.

In tiered 1 risk assessment, PCP exposure concentrations at different pH values were standardized to that at pH 7.8. Then, HQs were calculated through standardized exposure concentrations divided by CCC (pH=7.8). Xing et al. (2012a) and (Yi et al., 2015) didn't make risk assessment for actual waterbodies in spite of derived PCP WQCs depended on pH. Jin et al. (2012), Xing et al. (2012b) and Zhang et al. (2012) indeed did risk assessments for PCP in Chinese surface water, but the direct use of PCP exposure concentrations rather than the standardized would under- or over-estimate the risk. Taking the Liaohe River of dry season for example, there were existing differences between the two groups of HQs (Table S3), and the percentages of sampling sites at different risk levels with two calculating methods of HQs were also different (Table S4). Therefore, standardized exposure concentrations were favorable to reduce the uncertainty of risk assessment. Similarly, predecessors have performed the risk assessments of copper (Brix et al., 2001; Rahman et al., 2014; Schuler et al., 2008) and cadmium (Burger, 2008; Hall et al., 1998; Hou et al., 2013), whose toxicity could be affected by hardness. However, these studies ignored the influence of hardness of actual waterbodies on ecological risk. Hence, this study provided a reference about assessing ecological risk of pollutants while their toxicity is related to water quality factors.

The risk levels in Taihu Lake and Liaohe River were illustrated though analyzing the spatial distribution of HQs (Fig. 5). Overall, the environmental risk of PCP was the least in Liaohe River in wet season but the highest in Liaohe River in dry season. As for the Liaohe River, the PCP risks were relatively high in the central and southern basin, while in Taihu Lake, PCP risks were higher in the north and the east of Taihu Lake.

As the tiered 1 risk assessment (HQ method) cannot account for the probability and degree of ecological risks, the probabilistic method (Tiered 2-4) were also applied (see below section).

3.2.2. Tiered 2 assessment

PCP exposure concentrations used by tiered 2 (the same for tiered 3 and tiered 4) were standardized to that at pH 7.8 and the standardized exposure concentrations in Taihu Lake and Liaohe River were compared with PCP toxicity data. The results showed that probabilities

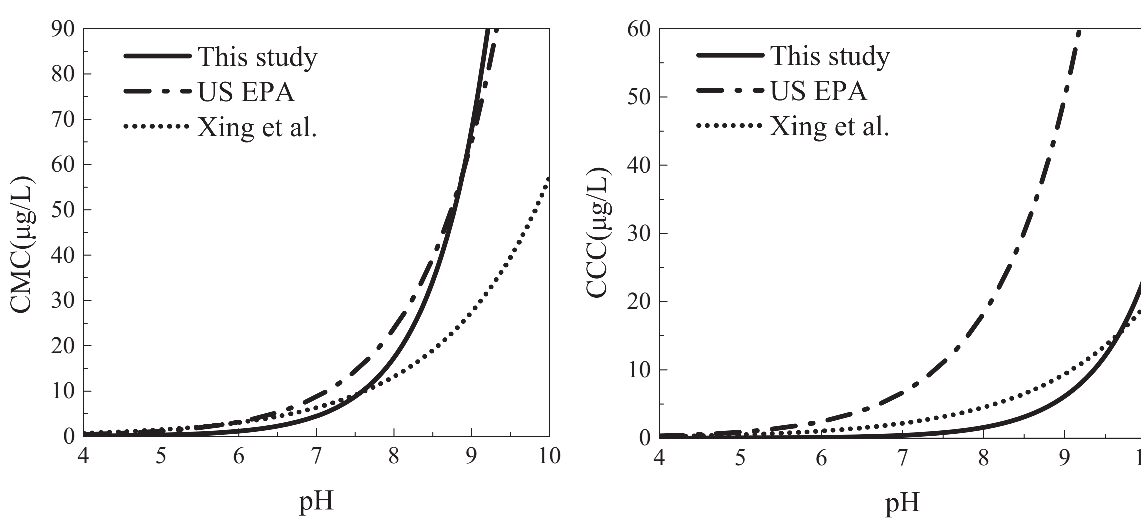

Fig. 4. Water quality criteria thresholds for PCP based on acute toxicity (CMC) and chronic toxicity (CCC) at different pH values.

Table 1
The HQs of PCP in Taihu Lake and Liaohe River.

Taihu Lake				Liaohe River						
Sampling sites	pH	Concentrations (μg/L)	HQ	Sampling sites	Wet season			Dry season		
					pH	Concentrations (μg/L)	HQ	pH	Concentrations (μg/L)	HQ
T1	8.97	0.96	0.16	L1	8.55	0.34	0.10	8.28	0.11	0.05
T2	8.75	0.14	0.03	L2	7.65	0.11	0.11	7.81	0.11	0.09
T3	8.81	0.07	0.02	L3	6.98	0.10	0.26	8.29	0.12	0.05
T4	7.79	0.15	0.13	L4	7.94	0.32	0.22	7.99	0.10	0.07
T5	8.65	0.12	0.03	*L5*	8.09	0.12	0.07	*8.28*	*2.92*	*1.28*
T6	8.77	0.38	0.09	L6	7.51	0.11	0.14	7.69	0.12	0.11
T7	8.75	0.14	0.03	L7	7.46	0.11	0.14	6.99	0.12	0.30
T8	8.25	0.87	0.39	*L8*	*7.91*	*1.68*	*1.21*	*7.60*	*4.24*	*4.64*
T9	8.91	0.99	0.18	L9	7.89	0.24	0.18	7.92	0.12	0.09
T10	8.68	0.14	0.03	*L10*	7.27	0.34	0.58	*8.04*	*2.21*	*1.33*
T11	*8.34*	*3.29*	*1.31*	L11	8.12	0.10	0.06	7.92	0.11	0.08
T12	7.70	0.24	0.23	L12	7.59	0.11	0.12	8.58	1.24	0.36
T13	8.16	0.59	0.30	L13	7.79	0.22	0.19	7.89	0.10	0.08
T14	8.38	0.43	0.16	*L14*	8.52	0.11	0.03	*8.48*	*3.72*	*1.22*
T15	8.61	0.74	0.21	*L15*	7.75	0.11	0.10	*7.67*	*3.34*	*3.34*
T16	8.41	0.49	0.18	L16	7.56	0.11	0.13	7.55	0.10	0.12
T17	9.46	0.03	0.00	L17	7.79	0.10	0.09	7.58	0.11	0.12
T18	8.90	0.17	0.03	L18	8.16	0.23	0.12	7.95	0.22	0.15
T19	7.54	0.14	0.17	L19	8.79	0.71	0.16	8.08	0.12	0.07
T20	7.75	0.07	0.07	*L20*	8.09	0.09	0.06	*8.70*	*6.73*	*1.64*
T21	7.61	0.11	0.12	L21	6.95	0.09	0.30	7.88	0.10	0.08
T22	7.51	0.49	0.61	L22	7.29	0.17	0.34	8.32	0.21	0.09
T23	8.98	0.61	0.10	L23	7.66	0.10	0.12	8.59	0.11	0.03
T24	8.47	0.57	0.19	L24	7.74	0.28	0.30	8.66	0.11	0.03
T25	8.40	0.15	0.05	L25	7.33	0.09	0.17	7.45	0.21	0.28
T26	8.37	0.34	0.13	*L26*	*7.43*	*0.66*	*1.09*	8.93	0.11	0.02
T27	8.54	0.06	0.02	**L27**	8.40	0.21	0.09	**7.37**	**8.65**	**12.92**
T28	7.85	0.54	0.42	L28	7.50	0.19	0.29	8.01	0.11	0.07
T29	*7.93*	*9.57*	*6.65*	L29	7.33	0.18	0.33	7.71	0.10	0.10
T30	8.32	0.25	0.10	L30	7.65	0.18	0.23	7.57	0.34	0.39
T31	8.05	1.13	0.67	L31	7.63	0.30	0.38	7.13	0.10	0.22
T32	8.10	0.37	0.21							
T33	8.02	0.82	0.50							
T34	8.12	0.45	0.24							
T35	8.22	0.13	0.06							
T36	8.40	0.82	0.30							
T37	8.53	0.50	0.16							

of PCP concentrations exceeding the CCC were not negligible—6.1%, 10.3%, and 2.1% in Taihu Lake, in the dry and wet season of Liaohe River, respectively. The risks of PCP in Liaohe river of wet season, Taihu lake and Liaohe river of dry season increased successively.

3.2.3. Tiered 3 assessment

As described above (Eq. (4)), MOS_{10} is a ratio calculated as the concentration of 10th percentile for toxicity effects divided by the concentration of 90th percentile for exposure distribution. The smaller MOS_{10} is, the greater the risk is. MOS_{10} of PCP in Taihu Lake, Liaohe River in the dry and wet season were 7.06, 10.38 and 4.66, respectively. Although all MOS_{10} were greater than one, there were still some areas where exposure concentrations of PCP were higher than CCC (Fig. 6; Fig. S2). These suggested that PCP in both surface waters of Liaohe River and Taihu Lake presented potential risks. PCP concentrations in Liaohe River in the dry

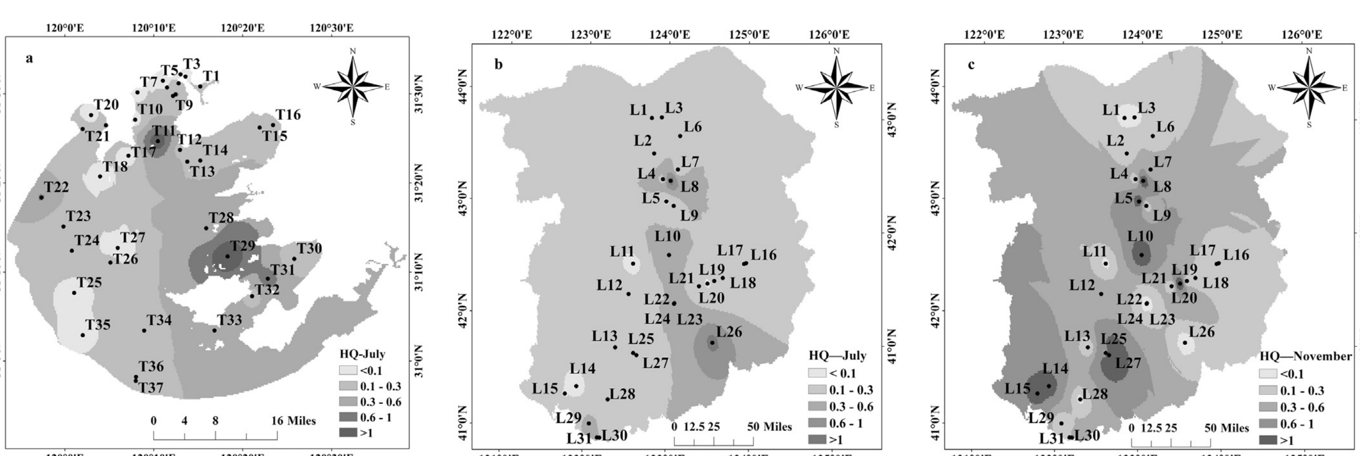

Fig. 5. The risk distributions of PCP based on HQs in Taihu Lake and Liaohe River. Fig. 5a is Taihu Lake; Fig. 5b and c are Liaohe River in the wet and dry season, respectively.

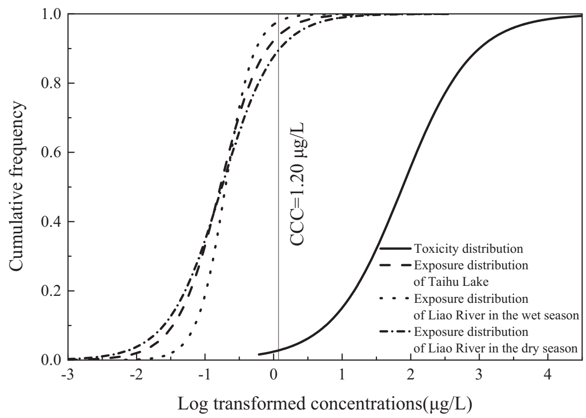

Fig. 6. Distribution of exposure concentrations of PCP at the three sites (stippled lines) contrasted with the chronic SSD for this chemical (solid line).

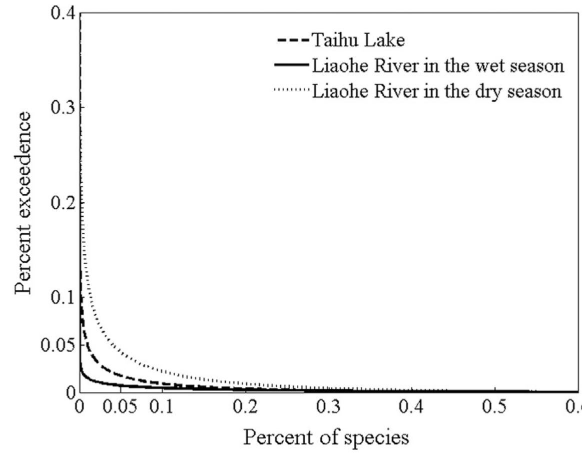

Fig. 7. Joint probability curves for ecological risk of PCP in surface water.

season had a greater ecological risk than Taihu and Liaohe River in the wet season.

Overall, the MOS_{10} method uses the information about toxicity distribution and exposure distribution. As only a deterministic value and the overall risk levels are provided, this method cannot provide a more comprehensive risk for PCP.

3.2.4. Tiered 4 assessment

Joint probability curve (JPC) constructed using exceedance probability function and SSD could better describe the general PCP risk (Fig. 7) than other risk assessment methods, and it is a more robust risk assessment method. The X axis of JPC represents the intensity of toxicity effects, and the Y axis stands for exceeded probability (Fig. 7). The PCP risk status could be visually revealed by JPC. The closer the JPC is to the X axis, the lower probability of PCP affecting the ecosystem. In this research, probabilities of exceeding NOEC for 1–5% of the species ranged from 1.79% to 4.98% for Taihu Lake, 0.76–1.51% for Liaohe River in the wet season and 4.32–11.84% for Liaohe River in the dry season. The results of JPC analysis indicated that the overall ecological environmental risk of PCP in Liaohe River in the dry season is the highest among the three sampling sites.

The results of all four tiered risk assessment were consistent with each other, and the PCP risk could be ranked as Liaohe River in the dry season > Taihu Lake > Liaohe River in the wet season. In China, PCP was widely used as a molluscicide to eradicate *Oncomelania* snails, particularly in Liaohe River and Yangtze River watershed (Taihu Lake is part of this watershed) (Gao et al., 2008). Besides, PCP is also used as a wood preservative in China (Zheng et al., 2000, 1997). In general, the degree of PCP contamination in Southern China in summer was more serious than in Northern China, which may be attributed to more extensive use of PCP in Taihu Lake than in Liaohe River (Gao et al., 2008). Meanwhile, in Liaohe River, the level of PCP pollution in the dry season was higher than that in the wet season. This was because the volume of water was reduced in the dry season, which may lead to the increase of PCP concentrations. The pH effect in this case could be ignored, as there is little change of pH values in the two seasons in Liaohe River (Independent-Samples *t* Test, $P > 0.05$).

Probabilistic methods generally serve to refine the risk estimated by the lower-tier approaches. Therefore, the results calculated from probabilistic methods can provide more useful information for decision makers. However, HQ, especially the single-value estimates, still have some advantages and can readily identify chemicals which have a potential capability to affect species, and it is also useful to focus risk assessment as a screening tool. The initial estimations in tiered 1 risk assessment show some high HQ values, which suggested some ecological risks in those areas. For purpose of getting a more reliable result, a number of researchers have recommended using a tiered approach from simple deterministic method to probabilistic method to characterize risk (Jin et al., 2012; Wang et al., 2009; Zolezzi et al., 2005).

3.3. Uncertainty analysis

Uncertainty in ERA using both determined HQ method and probabilistic risk method is inevitable. The uncertainty originated from the variations in PCP exposure concentrations in a specific sampling site and reported PCP toxicity data, the method of selecting species, risk models and other unknown factors (Chen, 2005). In particular, information on temporal and spatial variation in PCP exposure concentrations especially in Taihu Lake was limited, which was a vital source of uncertainty. To more precisely describe PCP exposures and as far as possible to decrease the uncertainty, further work should be conducted to get more PCP exposure data in a wide range of temporal and spatial scales. In addition, PCP chronic toxicity data of native organisms including twenty numbers of species belonging to five taxa, were used to construct SSD curve, and from which CCC of PCP were derived. Combined with the normalization of toxicity and exposure data based on pH, they were all effective ways to reduce present uncertainty. The major difficulty in the present study was the lack of PCP chronic toxicity data for Chinese species at different pH values - only one species (*Scenedesmus obliquus*) was found. Thus, the correlations between pH and toxicity data could not be established, and the slope of chronic toxicity related to pH was assumed equivalent to that of acute toxicity. Therefore, chronic toxicity experiment of PCP should be done to obtain more chronic data for native species at different pH values.

4. Conclusions

The toxic potencies of PCP to aquatic species were inversely proportional to pH values, so the smaller pH values are, the greater PCP toxicity is. Derived WQC including CMC and CCC were expressed as functions of pH. The CMC and CCC were 13.21 μg/L and 1.20 μg/L for normalized pH value of 7.8. Besides, a four-level tiered approach was used to assess the PCP risk in this study. Probabilistic risk assessments (PRAs) are useful tools to conduct the risk assessment for poisonous and harmful pollutants, and have an advantage over the determined HQ method. Because pH was a key factor in the risk assessment of this chemical, all PCP exposure concentrations were standardized to that at pH 7.8 to reduce the uncertainty. The results from all tiers of the ERA methods were consistent with each other, and PCP risk levels can be ranked as Liaohe River in the dry season > Taihu Lake > Liaohe River in the wet season. We wish this work would be helpful to support decision-making aiming to effectively minimize the PCP risk level in Taihu Lake and Liaohe River.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2016.09.023.

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