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Ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the water from a large Chinese lake based on multiple indicators

Ning Qin, Wei He, Xiang-Zhen Kong, Wen-Xiu Liu, Qi-Shuang He, Bin Yang, Hui-Ling Ouyang, Qing-Mei Wang, Fu-Liu Xu*

MOE Laboratory for Earth Surface Processes, College of Urban & Environmental Sciences, Peking University, Beijing 100871, China

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ABSTRACT

In the surface water of Lake Chaohu, China, the concentrations of 16 priority polycyclic aromatic hydrocarbons (PAHs) were measured by gas chromatograph–mass spectrometer (GC–MS). Based on the species sensitivity distribution (SSD) model and the probabilistic risk assessment (PRA) model, the indicators were calculated to assess the potential ecological risk of the individual and of multiple congeners of PAHs and their probabilities. The results revealed that the average residual level of the total PAHs (PAH_{16}) in the water ranged from 95.2 to 370.1 ng/L, with a mean value 181.5 ± 70.8 ng/L. The PAH content in the water was dominated by the low-molecular-weight congeners. The multi-substance potentially affected fractions (msPAFs) of the studied PAHs obtained by the SSD model varied from 0.29% (site B3) to 1.58% (site B6), with an average of 0.51 ± 0.34%. The average of the msPAFs (0.93%) for the inflow rivers was greater than that for the western (0.42%) and eastern (0.34%) parts of the lake. The greatest ecological risk probability calculated by the PRA model was found for Pyr (1.55%), followed by Ant (7.07×10^{-2}%), Fla (2.21×10^{-2}%), Phe (9.25×10^{-6}%), Nap (1.01×10^{-5}%), Flo (1.16×10^{-14}%) and Ace (2.86×10^{-16}%). The same order of ecological risks calculated by the two models was found for the studied PAH compounds. The toxicity data might be the primary source of the ecological risk uncertainties, as indicated by the greater values of coefficients of variation (CV) for the toxicity. This study concluded that the combinations of multiple indicators based on the SSD and PRA models for the ecological risk assessment are necessary to provide more general information on the spatial variations and the probabilities of potential ecological risks of the individual and multiple congeners of PAHs.

1. Introduction

An ecological risk assessment has been defined as the process of estimating the likelihood that a particular event will occur with a given set of circumstances (Maltby et al., 2005; Domene et al., 2008). During recent decades, some indicators and methods of different complexities have been proposed for the ecological risk assessment of toxic chemicals in water. In the early stages of a risk assessment, the hazard quotient (HQ), which is the quotient of the measured or estimated environmental concentration divided by the toxicant reference value, was proposed for the individual-value estimate (Solomon et al., 2000). The species sensitivity distribution (SSD) approach is one frequently used method for ecological risk assessment (Solomon et al., 1996; Steen et al., 1999). A SSD model is a statistical distribution describing, among a set of species, the variation in toxicity of a certain compound or mixture (van Straalen, 2002). To assess the eco-risk of toxic pollutants using the SSD model, some indicators, such as the maximum permissible concentration (MPC), negligible concentration (NC), potential affected fraction (PAF), hazardous concentration at which p% of the selected species will be affected (HC_p) and margin of safety (MOS10) can be calculated for both the ecological risk of an individual chemical and the combined ecological risk of multiple substances (Solomon et al., 1996; Steen et al., 1999). The SSD method has been proven as a useful site-to-site estimate both for the eco-risk of individual chemicals and for the joint eco-risk of multiple substances (Solomon et al., 1996; Steen et al., 1999). Although significant progress and improvements have been made for the SSD methods, there are still some flaws (e.g., the lack of uncertainty analysis) (Solomon et al., 2000; Forbes and Calow, 2002). To address this issue, a probabilistic risk assessment (PRA) was proposed (Solomon and Sibley, 2002). The PRA method considers the estimate of uncertainty and the stochastic properties of exposure and effects, and it allows the variability of exposure concentrations and the distributions of species sensitivity in the risk assessment process. It can better describe the likelihood exceeding the effect thresholds and the risk of adverse effects (Solomon and Sibley, 2002; Yang et al., 2006). The indicators, including the overlap area between the exposure and effect

* Corresponding author. Tel.: +86 10 62751177; fax: +86 10 62751187.
E-mail address: xufl@urban.pku.edu.cn (F.-L. Xu).

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curves, and the joint probability are calculated by the PRA method to assess the ecological risks (Wang et al., 2002; Shi et al., 2004). The PRA method has proven very useful in estimating both the exposure of a population or community to potentially hazardous pollutants and their responses to the chemicals in the research area (Wang et al., 2002). However, the PRA method requires as many measured data as possible to construct the probabilistic distribution of the exposure levels. The combinations of multiple risk indicators based on the SSD and PRA models for the ecological risk assessment are necessary to provide the more general information on the spatial variations and on the probabilities of the potential ecological risks of the individual and multiple pollutants.

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous persistent organic pollutants that are generally formed by the incomplete combustion of fossil fuels and biomass fuels (Rogge et al., 1993; Tao et al., 2005; Xu et al., 2006). PAHs are a major concern because of their potentially toxic, mutagenic, and carcinogenic properties (Khalili et al., 1995; Fernandes et al., 1997; Larsen and Baker, 2003; Li et al., 2009). The U.S. Environmental Protection Agency (USEPA) has established 16 PAHs as the priority control pollutants, and 7 of them are potentially carcinogenic to humans, according to the International Agency for Research on Cancer. Furthermore, PAHs enter a water body through wastewater discharge, surface runoff, atmospheric deposition and other means, such as crude oil leaks (Heemken et al., 2000). PAHs can adversely affect not only human health (through drinking water and skin contact) but also aquatic ecosystems. The ecological health risks of PAHs are being increasingly studied by environmental researchers. In China, PAHs emissions in excess of 27,000 tons/year have resulted in the contamination of various environmental media (Zhang et al., 2007). Lake Chaohu, the fifth-largest freshwater lake in China, is located near the Yangtze River delta region (Fig. 1), one of the most developed regions in China. With the rapid urbanization of the surrounding area, Lake Chaohu is becoming increasingly polluted by PAHs from human activities, such as the burning of fossil fuels and agricultural and industrial practices. This pollution will damage the lake ecosystem and compromise the safe use of the lake water as a water source for drinking, industrial production and agricultural irrigation. However, there is little information on the residual levels and ecological risks of PAHs in the water from Lake Chaohu.

There are three primary objectives of this study: (1) to investigate the residual levels and distributions of 16 priority PAHs in the water; (2) to estimate the potential ecological risk of the individual and multiple congeners of PAHs, based on both the SSD and PRA methods; and (3) to discuss the uncertainty of the ecological risks of the studied PAH components. A platform, named the Bayesian Matbugs Calculator (BMC), was developed to perform the best fittings of the distribution model, the ecological risk index calculations and the uncertainty analysis.

2. Methodology

2.1. Measurement of PAHs contents in the water

Water samples from 15 sites (Fig. 1) were collected in August 2009. An emphasis was placed on the eastern drinking-water source area with six sites (A6, B2, B3, B4, B5 and B7) and the inflow rives with four sites (C1, C2, C4 and B6). Twenty liters of water was collected from each sampling site. After shaking and mixing, a 1-L aliquot of each collected water sample was filtered through a 0.45-μm glass fiber filter (burned at 450 °C for 4 h) using a filtration device consisting of a peristaltic pump (80EL005, Millipore Co., USA) and a filter plate with a diameter of 142 mm. Surrogate standards of 2-fluoro-1,1′-biphenyl and p-terphenyl-d14 (J&K Chemical, USA, 2.0 mg/mL) were added to the water samples to indicate the recovery before extraction.

The water samples were extracted using a solid phase extraction (SPE) system (Supelco). C18 cartridges (500 mg, 6 ml, Supelco) were prewashed with dichloromethane (DCM) and conditioned with methanol and de-ionized water. A 1-L water sample passed through the SPE system and was extracted. The cartridges were eluted with 10 ml of dichloromethane. The volume of the extracts was reduced by a vacuum rotary evaporator (R-201, Shanghai Shen Sheng Technology Co., Ltd., Shanghai, China) in a water bath and was adjusted to a volume of 1 ml with hexane. Internal standards (Nap-d8, Ace-d10, Ant-d10, Chr-d12 and Perylene-d12) were added for the GC analysis.

All samples were analyzed on a gas chromatograph with a mass spectrometer detector (Agilent 6890GC/5973MSD). A 30 m × 0.25 mm i.d. with a 0.25-μm film thickness HP-5MS capillary column (Agilent Technology) was used. The column temperature was programmed to increase from 60 °C to 280 °C at 5 °C/min and then was held isothermal for 20 min. The MSD was operated in the electron impact mode at 70 eV, and the ion source temperature was 230 °C. The mass spectra were recorded using the selected ion monitoring mode. The concentrations 16 PAHs were determined: naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorine (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h) anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP) and benzo(g,h,i) perylene (BghiP).

The quantification was performed by the internal standard method using Nap-d8, Ace-d10, Ant-d10, Chr-d12 and Perylene-d12 (J&K Chemical, Beijing, China). All of the solvents used were HPLC-grade pure (J&K Chemical, Beijing, China). All of the glassware was cleaned using an ultrasonic cleaner (KQ-500B, Kunshan, China) and heated to 400 °C for 6 h. In the sampling process, three parallel samples were been collected from each sample site. The laboratory blanks were analyzed with the true samples. The average recovery for Nap, Ace, Acy, Flo, Phe, Ant, Fla and Pyr ranged from 75% to 117%, and for BaA, Chr, BbF, BkF, BaP, DahA, IcdP and BghiP was 68%, 67%, 54%, 51%, 77%, 45%, 34% and 35%, respectively. The detection limits were in the range of 0.54–4.22 ng/L.

2.2. Ecological risk assessment

The multiple risk indicators based on both the SSD and PRA models were calculated to obtain a comprehensive picture of the potential ecological risks of the PAHs in the water from Lake Chaohu. The SSD method (Wheeler et al., 2002; Liu et al., 2009; Wang et al., 2009a,b) was used for the site-specific assessment of the ecological risk for both the individual and multiple congeners of PAHs, while the PRA method was used for the probabilistic assessment of the ecological risk of individual PAH congeners based on all of the sampling sites.

2.2.1. General procedures of the SSD and PRA methods

The basic assumption of the SSD method is that the sensitivity of a group of organisms can be described by a distribution and that the available toxicological data are considered to be a sample of this distribution. Thus, the SSD is estimated from the sample of toxicity data and visualized as a cumulative distribution function. Both the acute (LC50, EC50) and chronic data (NOEC50) can be used to build the SSD; the acute data (LC50, EC50) was used in this study. To assess ecological risk using the SSD method, there are usually four steps: (1) obtain the toxicity data of the pollutants; (2) fit the SSD curves; (3) calculate the PAFs of the individual pollutants for the ecological risk assessment of an individual pollutant; and (4) calculate the accumulated multi-substance potentially

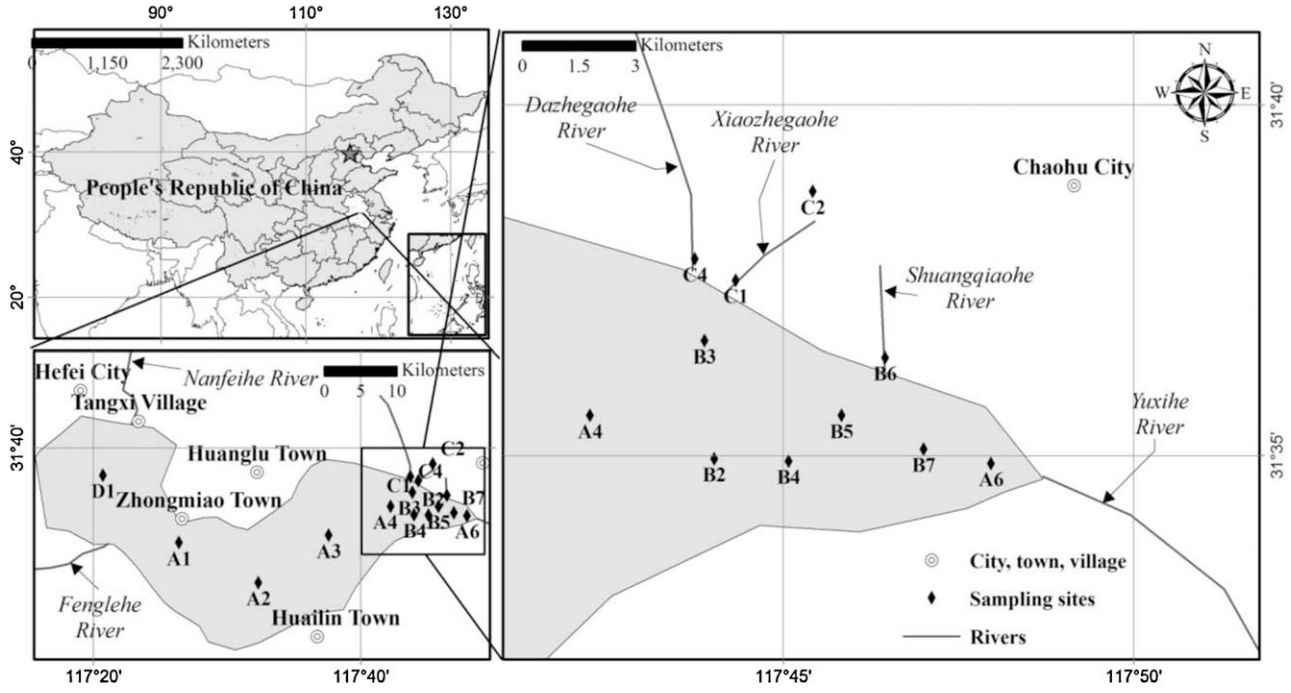

Fig. 1. Location of Lake Chaohu and water sampling sites, fifteen sites belongs to river sites (C1, C2, C3, C4), West Lake (D1), East Lake (A1, A2, A3, A4), and water source area (A6, B2, B3, B4, B5 and B7).

affected fractions (msPAFs) for the joint ecological risk assessment of multiple pollutants.

In contrast to the SSD method and focusing on the potential risk of an individual sampling site, the probabilistic risk assessment (PRA) method determines the ecological risk of pollutants through the analysis of the probability distribution curves of the toxicity and exposure levels in the entire lake. In the same manner as the SSD method, the toxicity data for all species are combined to produce an effect distribution curve; in addition, the exposure levels are plotted on the same axes as the toxicity effects data. The extent of overlap between the toxicity and exposure curves indicates the probability of exceeding an exposure concentration associated with a particular effect probability of the substance of concern. The use of the distribution curves for the exposure and toxicity data allows for the application of a joint probability curve (JPC) to describe the nature of the risks posed by the environmental concentrations measured. To assess the ecological risk using the PRA method, there are generally four steps: (1) obtain the toxicity data and exposure data of the pollutants; (2) fit the distributions of the toxicity data and exposure levels; (3) calculate the overlap area of the toxicity and exposure distribution curves for the ecological risk assessment of an individual pollutant; and (4) produce the joint probability curves of the pollutants for assessing the ecological risk probability of exceeding an exposure concentration associated with a particular effect probability.

The SSD and PRA methods have the same steps: collecting the toxicity data, fitting the distribution curves of the toxicity data, calculating the risk-index and estimating the ecological risk.

2.2.2. Collecting toxicity data

Based on the availability of the toxicity data, the studied PAH compounds included naphthalene (Nap), acenaphthylene (Ace), fluorine (Flo), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), fluoranthene (Fla), and benzo[a]pyrene (BaP). The toxicity data for these PAH compounds were collected from the database ECOTOX provided by the USEPA (www.epa.gov/ecotox). The 24- to 96-h acute toxicity data (LC50 or EC50) of the 8 PAHs to multiple aquatic species were collected. The species include green algae (*Selenastrum capricornutum*), a diatom (*Skeletonema costatum*), the southern house mosquito (*Culex quinquefasciatus*), the yellow fever mosquito (*Aedes aegypti*), a water flea (*Daphnia magna*), the sheepshead minnow (*Cyprinodon variegatus*), the channel catfish (*Ictalurus punctatus*), the brown trout (*Oncorhynchus mykiss*), the fathead minnow (*Pimephales promelas*), a scud (*Gammarus annulatus*), a freshwater prawn (*Palaemonetes*), and a pond snail (*Physa heterostropha*). The toxicity data of the 8 PAH compounds are presented in Table 1.

Both the acute data (e.g. LC50 and EC50) and chronic data (e.g. NOEC) of ecotoxicity can be used to build the SSD. However, in the present study, only the acute ecotoxicity data was used to build the SSD of PAHs based on the following two reasons. First, there were very limited chronic ecotoxicity data available for the studied PAHs. The amount of data is too small to easily generate a large deviation. The least amount of ecotoxicity data for the development of SSD model was five (Hose and Van den Brink, 2004) or eight (Wheeler et al., 2002). Second, some studies developed the chronic SSD model using the chronic ecotoxicity data that converted from the acute data based on the empirical formula (e.g. Heger et al., 1995; Lange et al., 1998). However, such approach on the basis of the empirical formula caused high uncertainty of the SSD curve, which lead further to the high uncertainty of assessment results as well.

2.2.3. Fitting the distribution of toxicity and exposure data

The PRA method requires a fit of the distributions of both the toxicity and exposure data, while the SSD method requires only a fit of the distribution of the toxicity data. In most cases, the exposure data are of a log-normal distribution. However, for the toxicity data, because no certain distribution has been proved theoretically (Wheeler et al., 2002), different distribution models have been selected, including log-normal (Wagner and Lokke, 1991), log-logistic (Aldenberg and Slob, 1993) and Burr Type III (Shao, 2000). To select the best SSD model, a platform named the Bayesian Matbugs Calculator (BMC) (He et al., submitted for publication) was

Table 1
Statistics of the toxicity data (LC50 or EC50) for eight individual PAHs (μg/L).

	Nap	Ace	Flo	Phe	Ant	Fla	Pyr	Bap
Minim	40.70	240.00	212.00	212.13	1.93	1.20	2.63	4.00
Maxim	175,927	3499	5800	195,697	17,822	41,590	894,000	17,660
Arithmetic mean	5020	660	1591	870	56	48	60	13
Geometric mean	4818	847	1340	1992	76	67	167	76
Standard deviation	37796	987	1967	1992	4278	7985	269027	6273
Total data number	24	11	12	17	17	27	11	12

developed based on the Bayesian Inference, WinBUGS software (Lunn et al., 2000; Ntzoufras, 2009) and Matlab graphical user interface (GUI). Five frequently used distribution modes, including the log-normal, log-logistic, BurrIII, Reweibull and Weibull models (van Straalen, 2002), were compared. The best fitting distribution mode was determined by the index of deviance information criterion (DIC) using the following equation:

$$\mathrm{DIC} = \bar{D} + p_D \tag{1}$$

$\bar{D}$ and p_D were used to measure the quality of the fit and the complexity of the model, respectively. The smaller the value of the DIC, the better the curve fit the toxicity data. In the WinBUGS software, the DIC value can be obtained directly by a Markov Chain Monte Carlo (MCMC) simulation. As shown in Table 2, the BurrIII model has the smallest values for Phe, Ant, Fla and Pyr; however, no significant differences in the DIC values for the different models were found by a one-way ANOVA test. The Kolmogorov–Smirnov tests revealed that both the toxicity and exposure data followed a log-normal distribution. Thus, a log-normal model was chosen to simulate the SSD curve of the PAH toxicity data. The parameters of the log-normal SSD distributions of the 8 PAHs are presented in Table 3.

2.2.4. Ecological risk assessment based on multiple risk indices

For the PRA method, the potential ecological risks were assessed by calculating the overlap area between the exposure and effect curves (Wang et al., 2002) and by calculating the joint probability curves (JPCs) (Shi et al., 2004). The JPCs can be obtained by plotting the cumulative probability distributions of the exposure and toxicity data for each chemical on the same axes. Each point on the curve represents both the probability that the chosen proportion of a species will be affected and the frequency with which that level of effect would be exceeded (Solomon et al., 2000; Wang et al., 2002).

For the SSD method, the potentially affected fraction (PAF) of the individual PAH compound and the accumulated potentially affected fractions of 8 PAH compounds (msPAFs) are used for the ecological risk assessments. The PAF was calculated by the following equation:

$$\mathrm{PAF} = \frac{1}{\sqrt{2\pi}\sigma_0} e^{-(([lg(C-\mu_0)]^2)/2\sigma_0^2)} \tag{2}$$

where C is the log-transformed exposure concentration of 8 specific PAHs, μ_0 is the mean value of the toxicity data, and σ_0 is the standard deviation of the toxicity data in Table 3.

The msPAFs are calculated based on the toxicological mode of action (TMoA) of the pollutants. In case where the pollutants had the same or similar TMoA, a concentration-addition method could be used to calculate the msPAF; otherwise, a response-addition approach will be used (Traas et al., 2002). Because the TMoA of PAHs is not currently clear, both the concentration-addition and response-addition approaches were used to calculate the msPAF in this study. The msPAFs of 8 PAHs were calculated by Eqs. (3)–(5) for the concentration-addition approach (Traas et al., 2002):

$$\mathrm{HU}_i = \frac{C_i}{\bar{C}_i} \tag{3}$$

$$\mathrm{HU}_{\mathrm{TMoA}} = \sum_i^n \mathrm{HU}_x \tag{4}$$

$$\mathrm{msPAF} = \frac{1}{\sqrt{2\pi}\sigma} e^{-(([lg(\sum \mathrm{HU}_{\mathrm{TMoA}})]^2)/2\sigma^2)} \tag{5}$$

where HU_i and $\mathrm{HU}_{\mathrm{TMoA}}$ are the dimensionless hazard units of the ith PAH component and of the addition of all HUs for the studied individual PAH components; C_i and $\bar{C}_i$ are the concentrations of the measured data and the geomean value of the toxic data of the ith PAH component (μg/L), respectively; and σ is the average standard deviation of the toxicity data of all studied individual PAH components (μg/L).

For the response-addition approach, the equation for calculating the msPAF of 8 PAHs is as follows (Traas et al., 2002):

$$\mathrm{msPAF} = 1 - \prod_i (1 - \mathrm{PAF}_i) \tag{6}$$

For $i = 1$ to n substances, msPAF represents the multisubstance potential affected fractions of the various compounds calculated by the response addition.

2.3. Uncertainty analysis

For the selected specific method for the assessment ecological risk, such as the SSD and PRA methods, the sources of uncertainty in the assessment results are mainly from the exposure level and toxicity data. The uncertainty in the exposure levels originates from the sampling and laboratory analysis errors. The toxicity data for the limited species cultured and tested in the laboratory extrapolated to the responses of natural taxa may lead to uncertainty because the laboratory LC50 values may overestimate the field effects at the population level. The lack of toxicity data also causes obvious uncertainty for the assessment results of the ecological risks.

A Monte Carlo simulation was used to demonstrate the uncertainties of the exposure and toxicity data. Both the exposure and toxicity data were represented as a probability density function that defined both the range of values and the likelihood of the data having that value. All of the data were assumed to follow the log-normal distribution. The simulation was performed 5000 times, with new values randomly selected for the data within the range of the mean ± standard deviation. The WinBUGS developed in this study were used to randomly select the values for the data. The uncertainty was ascertained by the statistical analysis of the output result. To quantify the differences, the coefficients of variation (CVs) were calculated based on the log-transformed data.

3. Results

3.1. Levels and distributions of PAHs in the water

The total PAH concentrations (PAH_{16}) (sum of the 16 EPA priority pollutants) in the water from Lake Chaohu are provided in Fig. 2. The total PAH concentrations in the 15 sample sites ranged from 95.2 ng/L to 370.1 ng/L, with a mean value 181.5 ± 70.8 ng/L. The

Table 2
Deviance information criterion (DIC) values of the five different models for the SSD fitting.

	Nap	Ace	Flo	Phe	Ant	Fla	Pyr	BaP
Log normal	484.1	178.4	212.0	335.0	228.9	339.9	175.3	163.4
Log logistic	482.2	179.0	212.9	335.0	229.4	333.6	172.3	169.8
Burr III	489.8	180.3	213.9	329.4	223.4	332.8	168.6	163.4
ReWeibull	492.3	188.6	219.3	331.6	227.7	340.4	170.3	169.8
Weibull	482.9	163.9	199.8	339.7	232.7	355.2	179.9	163.4

Table 3
SSD parameters of the toxicity data and exposure levels of eight individual PAHs (μg/L).

	Nap	Ace	Flo	Phe	Ant	Fla	Pyr	BaP
μ_0	3.683	2.928	3.127	3.299	1.882	1.825	2.222	1.879
σ_0	0.758	0.356	0.471	0.915	1.056	0.802	1.568	1.458
μ_1	−1.163	−2.110	−1.692	−1.370	−2.551	−2.041	−2.041	−4.026
σ_1	0.159	0.222	0.155	0.153	0.274	0.255	0.280	0.333

μ_0 and σ_0 as well as μ_1 and σ_1 with μg/L as unit are the mean values and standard deviations for the log-transformed toxicity data and for the log-transformed exposure data, respectively.

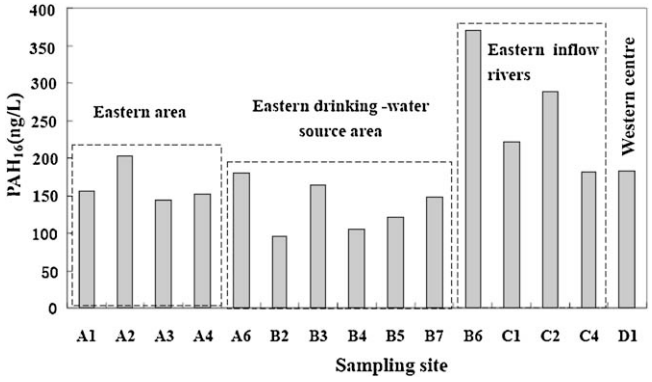

Fig. 2. Distributions of total PAHs (PAH_{16}) in the water from Lake Chaohu.

highest level of total PAHs was detected at site B6, the Shuangqiao River, and the second highest level was at site C2, the Xiaozhigao River. With a mean value of 267.3 ± 80.0 ng/L, the total PAH concentration in four of the river sites was much greater than that in the lake, which had a mean concentration of 150.3 ± 32.9 ng/L. Inside the lake, the maximum PAH level was found in the western lake (183.1 ng/L), followed by the eastern lake (excluding the water source area) (163.8 ± 23.3 ng/L) and then the eastern water source area (135.8 ± 30.4 ng/L). Of the 16 priority PAHs, Nap had the highest concentration (68.8 ng/L), followed by Phe, Flo, Fla, Pyr, Ant and Acy, with concentrations of 42.7, 20.3, 9.1, 9.1, 2.8 and 1.2 ng/L, respectively. The concentrations for the rest of the 16 priority PAHs were less than 1 ng/L. Fig. 3 shows that the content of the low-molecular-weight PAHs were much greater than that of the high-molecular-weight PAHs.

3.2. Ecological risk assessment

3.2.1. Site-specific ecological risk of PAHs based on the SSD method

The exposure concentrations of 8 individual PAHs for each sampling site were translated into the ecological risk values based on the SSD curves. The risks of concentration-addition and response-addition msPAFs were also calculated to represent the combined ecological risk of the 8 PAHs. The results are listed in Table 4.

Table 4 revealed that the HMW PAHs have greater risks than the MMW PAHs: Pyr had the greatest ecological risk with PAFs ranging

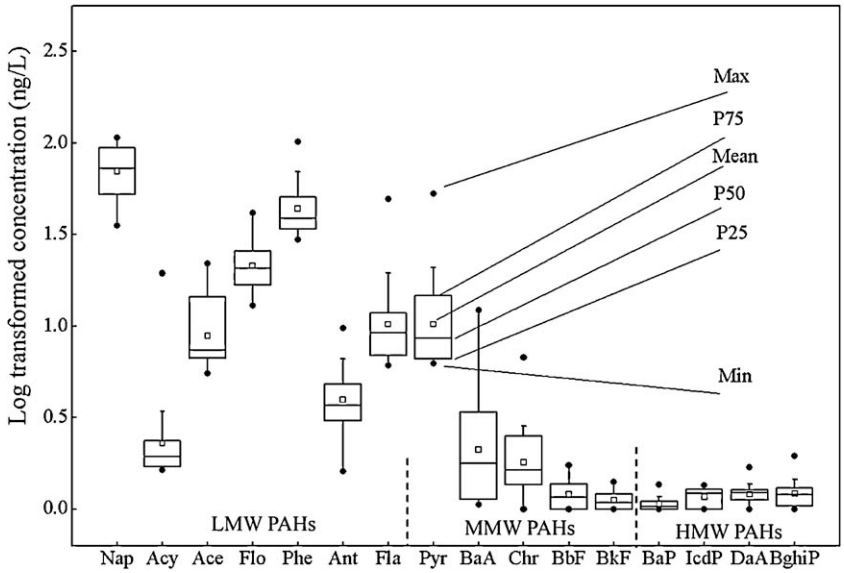

Fig. 3. Contents of 16 PAHs in the water from Lake Chaohu. LMW PAHs include Nap, Acy, Ace, Flo, Phe, Ant and Fla, MMW PAH includes Pyr, BaA, Chr, BbF and BkF, and HMW PAHs include BaP, IcdP, DahA and BghiP. The vertical axis is log-transformed total PAH concentrations $\log(C_{PAHs} + 1)$.

Table 4
Potentially affected factions (PAFs) for eight individual PAHs at fifteen sample sites.

Sampling site	PAFs for eight individual PAHs (%)								msPAF (%)	
	Nap ($\times10^{-9}$)	Ace ($\times10^{-43}$)	Flo ($\times10^{-23}$)	Phe ($\times10^{-5}$)	Ant ($\times10^{-4}$)	Fla ($\times10^{-5}$)	Pyr ($\times10^{-1}$)	BaP ($\times10^{-5}$)	Con-add ($\times10^{-3}$)	Res-add ($\times10^{-1}$)
A1	9.02	49.06	321.95	3.04	27.35	8.73	4.20	–	6.12	4.23
A2	72.83	135.88	662.05	3.46	32.57	6.30	3.47	9.04	5.88	3.60
A3	16.60	0.41	28.57	1.83	1.13	6.02	3.03	–	3.25	3.03
A4	31.91	7.55	22.16	1.29	10.72	2.45	2.93	–	2.85	2.95
A6	64.68	68.27	124.10	1.70	11.35	3.07	3.11	5.26	3.50	3.18
B2	1.16	0.16	1.23	1.06	6.54	3.18	2.97	–	2.45	2.97
B3	42.56	52.98	45.29	1.48	11.11	2.43	2.85	–	2.95	2.86
B4	2.25	17.63	3.53	1.17	10.92	2.02	3.09	–	2.43	3.10
B5	2.26	105.36	17.05	2.09	15.69	7.40	3.84	20.30	4.86	4.06
B6	27.86	2.91×10^{9}	6.43×10^{4}	20.57	127.59	555.19	15.61	1.05	85.10	15.80
B7	5.40	1.86	123.25	3.29	29.28	7.73	4.41	2.01	5.96	4.46
C1	18.22	6.81×10^{-6}	6.38×10^{3}	6.90	62.36	32.40	7.23	4.69	16.22	7.35
C2	46.47	5.42×10^{-9}	2.88×10^{4}	8.67	58.22	59.72	7.99	–	22.19	8.06
C4	14.26	2.52×10^{7}	964.31	4.03	32.42	15.49	6.04	4.69	10.02	6.12
D1	68.56	9.78	10.79	1.65	17.90	10.32	4.18	2.52	6.03	4.23
Mean	28.27	5.57×10^{8}	6783.03	4.15	30.34	48.16	5.00	6.20	11.99	5.07
GM	15.48	1007.07	156.78	2.77	18.70	9.38	4.37	4.28	6.35	4.43

from 2.85×10^{-3} (B3) to 1.56×10^{-2} (B6). The average risk of Pyr is two orders of magnitude greater than that of Ant, three orders of magnitude greater than that of Fla, and four orders of magnitude greater than those of Phe and BaP. The LMW PAHs have the least ecological risk; Nap risks were twelve orders of magnitude greater than Flo and twenty-seven orders of magnitude greater than the risks of Ace, which had the least ecological risk 1.61×10^{-46} (B2) to 2.91×10^{-36} (B6) with a mean of 5.57×10^{-37}. The results can be attributed to the major toxicity of the HMW PAHs and the significant concentrations of the MMW PAHs.

The msPAFs of the response addition ranged from 2.86×10^{-3} (B4) to 1.58×10^{-2} (B6), and the msPAF of the concentration addition varied from 2.43×10^{-5} (B4) to 8.51×10^{-4} (B6). The msPAFs based on concentration were even lower than the PAFs of some individual PAHs, such as Pyr, which indicates that the risks based on concentration are underestimated. The concentration addition can be applied based on the hypothesis that the chemicals that have the same toxicity mode so that the exposure data can be scaled into dimensionless hazard units (HUs). In other words, the chemicals have similar distribution modes and the same variance (Traas et al., 2002). However, the PAH toxicity data have quite different standard deviations (Table 3). There may be two reasons for this: first, the PAHs may have different toxicity modes in the water system, so the concentration-addition method should not be used in the water ecological risk assessment, and second, there are insufficient data to form the complete distribution curves. Before the toxicity mode was clear, the msPAF based on the response addition may be a credible result.

The results of the response-addition msPAF are used to analyze the geographical risk distribution of the PAHs in Lake Chaohu. The msPAF in Lake Chaohu ranged from 0.29% (B3) to 1.58% (B6). The ecological risks in rivers, with mean value 0.93%, were greater than those in the lake, where the mean PAF value was 0.35%. Site B6 had the largest PAF value (1.58%), which is 2.0 times greater than the ecological risk in the upstream of the Xiaozhigao River, 2.2 times greater than that in the estuary of the Xiaozhigao River, and 2.6 times greater than that in Dazhigao River. In the lake, the mean value of the PAF in East Lake (0.34%) was less than the PAF in West Lake (0.42%) and was at the same level as that in the water source area (0.34%). The result indicated that rivers may be the main sources of the PAHs pollution in Lake Chaohu. Controlling the PAH discharge into the river inflows may be important to control the PAH pollution in Lake Chaohu.

3.2.2. Probability of ecological risk of PAHs based on the PRA method

The toxicity and exposure distribution curves of 7 PAHs were produced. The BaP level was lower than the detection limit in 7 sites; thus, BaP was not included due to a lack of exposure data. The ecological risks of the exposure PAHs in Lake Chaohu were qualified by the calculation of the overlap area *S* (Fig. 4). The black line is the distribution of the log-transformed exposure values, and the red line is the distribution of the log-transformed toxicity values. The risks based on the PRA method ranged from 2.86×10^{-16}% to 1.55%. The greatest ecological risk probability was found for Pyr (1.55%), followed by Ant (7.07×10^{-2}%), Fla (2.21×10^{-2}%), Phe (9.25×10^{-6}%), Nap (1.01×10^{-5}%), Flo (1.16×10^{-14}%) and Ace (2.86×10^{-16}%).

A joint probability curve (JPC) for each chemical was generated (Fig. 5). The position of the joint risk probability curve reflects the risk of the PAHs; the closer the curve is to the axis, the less risk the chemical poses. The JPC of the 7 PAHs demonstrates that the risk gaps between the PAHs are quite large. Fla and Ant were plotted on the same scale, Pyr was plotted on a large-scale axis, and the other four PAHs were plotted on a smaller-scale axis. As the results from the overlapping area calculation, Pyr caused the greatest risk among the compounds studied, followed by Ant, Fla, Phe, Nap, Flo and Ace. The order was the same as that calculated by the overlap area and the average risk values by SSD.

4. Discussions

4.1. Comparisons of PAHs levels in the water with previous studies

The PAH_{16} in the inflow rivers to Lake Chaohu (267.3 ± 80.0 ng/L) was close to that found in the Tianjin rivers (281.6 ± 336.9 ng/L) (Shi et al., 2004) and was less than that reported in the Yangtze River (0.242–6.235 μg/L) (Feng et al., 2007) and greater than that found in the Yellow River (121.3 ng/L) (Wang et al., 2009a,b) and in the Luan River (99.4 ng/L) (Cao et al., 2010). The PAH_{16} in Lake Chaohu (150.3 ± 31.4 ng/L) was close to that reported in Lake Taihu (134.5 ± 54.8 ng/L) and greater than that reported in the Pearl River Estuary (Luo et al., 2006). Compared with reports from abroad, the PAH_{16} level in Lake Chaohu was lower than the levels in Victoria Lake (Kwach and Lalah, 2009), Great Bitter Lake and El Temsah Lake (Said and El Agroudy, 2006).

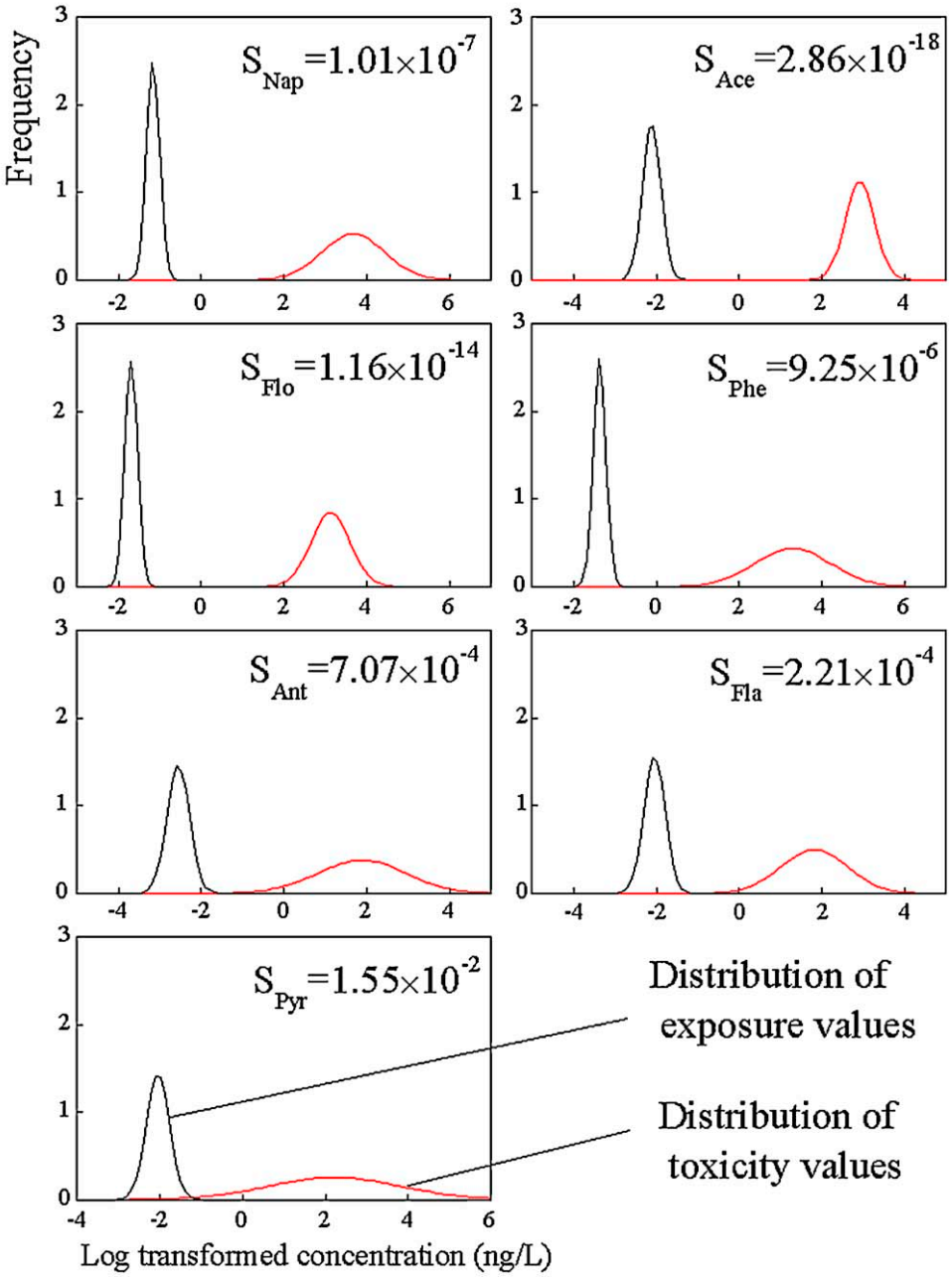

Fig. 4. Toxicity and exposure distribution curves of seven PAHs.

4.2. Comparisons of ecological risks based on the SSD and PRA methods

The comparisons of the ecological risk assessment results of the seven PAHs based on the SSD and PRA methods are presented in Fig. 6. The ecological risks calculated by the SSD and PRA methods were not of the same order of magnitude, and the risks estimated by the PRA method were greater than those estimated by the SSD method. However, the ecological risk orders of seven PAHs were the same. A significant difference was identified in the Ace ecological risks produced by the two methods. This might be caused by the uncertainty that exists with the Ace data (see next section for details).

4.3. Uncertainty analysis

Monte Carlo simulation was used to demonstrate the uncertainties of the exposure and toxicity data. The more simulation times performed, the closer the results obtained to the real situation. The simulation times 1000, 3000, 5000 and 10,000 iterations commonly used in the literatures. In the present study, the results based on the simulation times 1000, 3000, 5000 and 10,000 iterations were compared, and showed that 5000 times iterations was sufficient enough to ensure the stability of results. For the simulation results, there were no statistically significant differences between 5000 and 10,000 times iterations.

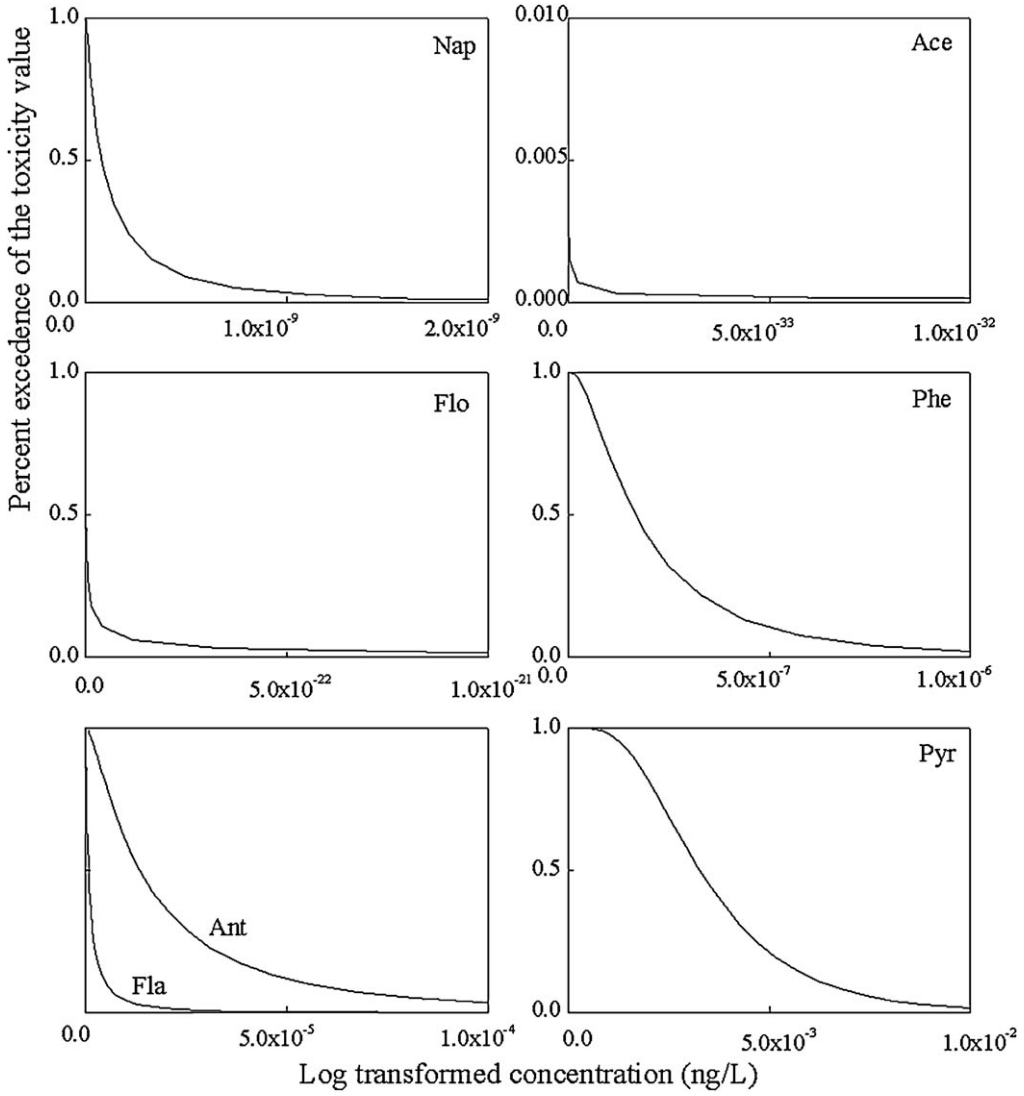

Fig. 5. Joint probabilistic curves of seven PAHs.

The comparisons of the CV values of the toxicity and exposure data for eight PAHs based on 5000 Monte Carlo simulations are presented in Fig. 7. The larger CV values were found for the toxicity data of eight PAHs, indicating the uncertainties were larger for the toxicity data than for those of the measured exposure data (Fig. 7). The CVs varied from 1.14 to 6.92 for the toxicity data, while the CVs were from 0.28 to 0.36 for the measured exposure data. For the toxicity data, Ace had the largest CV value (6.92), followed by Flo (4.94), Nap (4.85), Phe (2.22), Fla (2.01), Ant (1.78), BaP (1.70) and

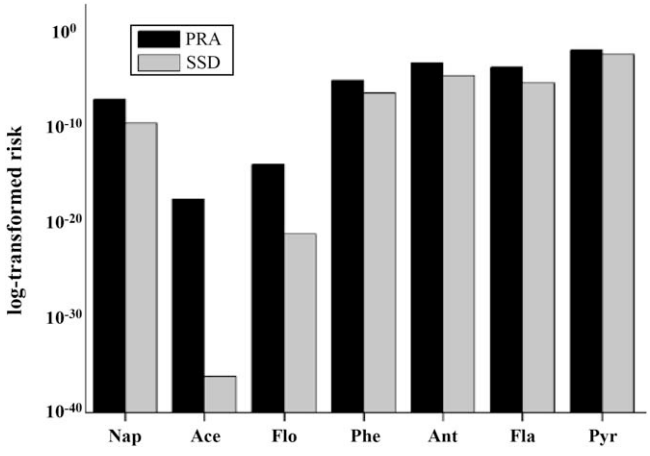

Fig. 6. Comparisons of ecological risk assessment results of seven PAHs based on the SSD and PRA methods.

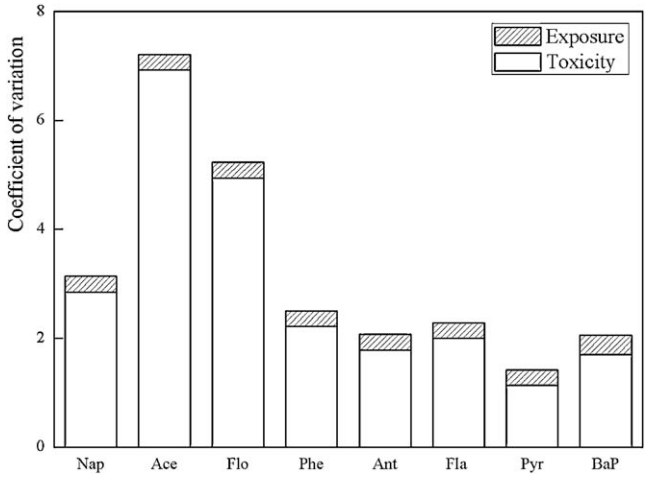

Fig. 7. Comparisons of CV values of the exposure data and toxicity data for eight PAHs.

Pyr (1.14). For the measured exposure data, BaP had the largest CV (0.36) because there were eight measured exposure values. Fig. 7 illustrates that the uncertainties of the exposure data of eight PAHs were very similar, as indicated by their CV values. This result suggested that the uncertainties of the toxicity data might be the primary source of the ecological risk uncertainties.

4.4. The advantages and disadvantages of the combination of the SSD and PRA methods

The combination of the SSD and PRA methods can provide the more general information on the spatial variations and on the probabilities of the potential ecological risks of the individual and multiple pollutants. The combination of the SSD and PRA methods can joint the advantages and overcome the disadvantages of the two methods used alone.

The SSD model can provide a site-specific risk assessment, and make it possible for the comparison of spatial distribution of ecological risks. Furthermore, the SSD model provides a method to calculate msPAFs of different contaminates. In contrast, the PRA method, introducing the concept of probability into the risk evaluation, considers the variability of exposure concentrations, and provides a probabilistic risk assessment for the whole area. In addition, the results from the PRA method can be illustrated in the joint probabilistic curves to reflect the relationship of exposure concentration and ecological risks which cannot be obtained by the SSD method.

The SSD and PRA methods have their disadvantages. First, both of the models are established on the probabilistic distribution of toxicity data, and depend on the adequacy of the toxicity data. As mentioned in the uncertainty analysis, the uncertainties were larger for the toxicity data than for the measured exposure data. Therefore, the toxicity data determine the reliability of the assessment results. Furthermore, the PRA method depends on the adequacy of the exposure data for the establishment of exposure distribution curve. Second, both methods have shortcomings in the estimation of msPAFs. The PRA method cannot be used in the evaluation of multi-risk assessment of different compounds. In contrast, although the msPAFs can be calculated based on two toxicological modes of action, it is still difficult to obtain the joint risk before the toxicological modes of action are clear. The response-addition msPAFs of the studied PAHs in Lake Chaohu, for example, was two orders of magnitude greater than the concentration-addition msPAFs. Clarifying the toxicological modes of action for different contaminants is necessary to calculate the msPAF of multi-contaminants.

5. Conclusion

Multiple indicators were calculated, and the ecological risks of PAHs were compared based on the SSD and PRA models. The combination of the SSD and PRA methods for the ecological risk assessment could provide the more general information on the spatial variations and the probabilities of the potential ecological risks of the individual and multiple congeners of PAHs. Determining the best fitting model for the toxicity and exposure data is a crucial step for the ecological risk assessment. Performing the fittings of the distribution model, the calculations of ecological risk index and the analysis of uncertainty with a platform such as the Bayesian Matbugs Calculator (BMC) developed in this study would be a great help. Of all of the PAH congeners, Pyr presented the greatest ecological risk, followed by Ant, Fla, Phe, Nap, Flo and Ace. The uncertainties of the toxicity data with the larger CV value might be the primary uncertainty source for the ecological risks.

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