

## Article

# Multi-Media Exposure to Polycyclic Aromatic Hydrocarbons at Lake Chaohu, the Fifth Largest Fresh Water Lake in China: Residual Levels, Sources and Carcinogenic Risk

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**Abstract:** The residual levels of 16 priority polycyclic aromatic hydrocarbons (PAHs) in environment media and freshwater fish were collected and measured from Lake Chaohu by using Gas chromatography-mass spectrometry. Potential atmospheric sources were identified by molecular diagnostic ratios and the positive matrix factorization (PMF) method. PAH exposure doses through inhalation, intake of water and freshwater fish ingestion were estimated by the assessment model recommended by US EPA. The carcinogenic risks of PAH exposure were evaluated by probabilistic risk assessment and Monte Carlo simulation. The following results were obtained: (1) The PAH<sub>16</sub> levels in gaseous, particulate phase, water and fish muscles were 59.4 ng·m<sup>-3</sup>, 14.2 ng·m<sup>-3</sup>, 170 ng·L<sup>-1</sup> and 114 ng·g<sup>-1</sup>, respectively. No significant urban-rural difference was found between two sampling sites except gaseous *BaP<sub>eq</sub>*. The relationship between gaseous PAHs and PAH in water was detected by the application of Spearman correlation analysis. (2) Three potential sources were identified by the PMF model. The sources from biomass combustions, coal combustion and vehicle emission accounted for 43.6%, 30.6% and 25.8% of the total PAHs, respectively. (3) Fish intake has the highest lifetime average daily dose (LADD) of 3.01 × 10<sup>-6</sup> mg·kg<sup>-1</sup>·d<sup>-1</sup>, followed by the particle inhalation with LADD of 2.94 × 10<sup>-6</sup> mg·kg<sup>-1</sup>·d<sup>-1</sup>. (4) As a result of probabilistic cancer risk assessment, the median ILCRs were 3.1 × 10<sup>-5</sup> to 3.3 × 10<sup>-5</sup> in urban and rural residents, which were lower than the suggested serious level but higher than the acceptable level. In summary, the result suggests that potential carcinogenic risk exists among residents around Lake Chaohu. Fish ingestion and inhalation are two major PAH exposure pathways.

**Keywords:** PAHs; multi-media exposure; health risk; probabilistic risk assessment; Lake Chaohu

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are globally concerned pollutants because of their widespread occurrence, strong persistence and long-range transportation potential [1]. Furthermore, they possess potential toxicity, mutagenicity and carcinogenicity [2–4]. Studies have shown that human cancer causes of skin, lungs and bladder have always been associated with PAHs [5–8], and 16 PAHs are included on the priority pollutants list of the

US EPA. PAHs have a wide variety of sources, including coal combustion, vehicle emission, coking industry and biomass burning [9–11]. After being emitted into the environment, PAHs may redistribute in environmental media and result in people being exposed to these pollutants through multiple pathways, including breathing in polluted air and particles, drinking water, dietary intake and dermal contact with contaminated soil [12,13]. Multi-media distribution and multi-pathway exposure render the assessment of PAH exposure complicated. Therefore, accurately evaluating the contribution of each exposure pathway, characterizing the carcinogenic risk and identifying the sensitive parameters in the exposure process are crucial to the management of PAH emission.

Water bodies act either as a sink [14] or as a source [15] for PAHs in the environment. The atmospheric PAHs can enter water system through wet deposition, dry deposition and gas exchange across the air–water interface [16–18]. Meanwhile, PAHs in water may accumulate in aquatic organisms by direct uptake from water through gills or skin or by the ingestion of suspended particles and contaminated food [19]. Residents living near the lake can be exposed to PAHs by inhaling polluted air and ingesting water and aquatic products.

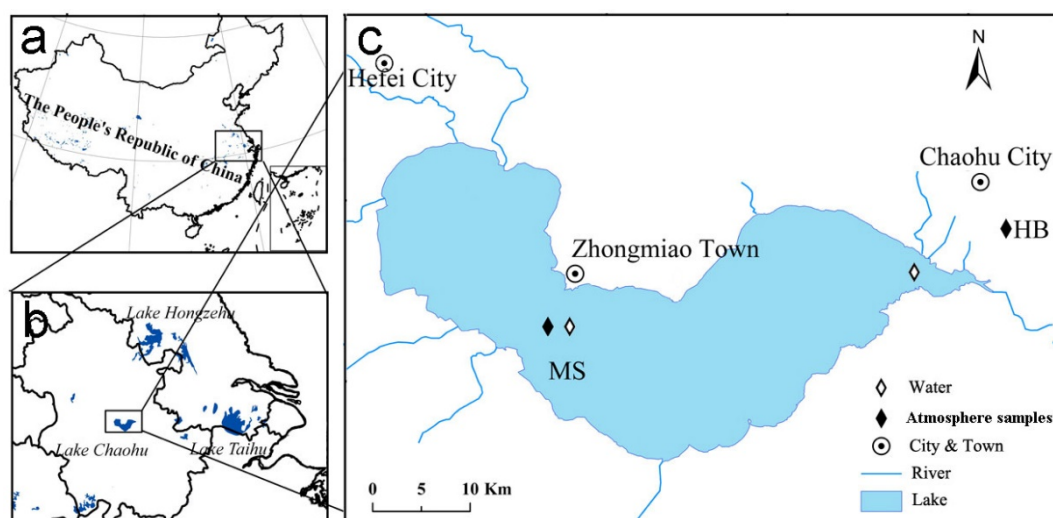
Lake Chaohu is located in the Anhui Province, which belongs to one of the most developed areas in China, Yangtze River Delta Economic Zone. During the last decades, the PAHs' emission in China, especially in the above-mentioned areas, increased greatly due to the increasing energy demand associated with rapid population growth and economic development and to the low efficiency of energy utilization [20]. Chaohu is famous for its fresh water fish. It is also the drinking water source of large cities such as Hefei and Maanshan. PAH pollution in water system of Chaohu may increase the risk of residents' exposure through fish ingestion and drinking water. Therefore, in recent years, PAH exposure in Lake Chaohu has become a topic of concern. Some studies have been conducted on the PAH residual levels in environment media, source apportionment or environment behaviors [21–25]. Despite the progress in these directions, studies on three issues remain scarce. First, comparison among exposure contribution from different pathways are seldom reported. Second, carcinogenic risk due to total exposure remains unclear. Third, the factors influencing risk assessment are seldom studied. Hence, further studies on PAHs should be performed in order to obtain a comprehensive understanding of the risk profile of PAHs exposure among Chaohu residents.

In this research, EPA priority control PAHs were selected as target chemicals due to their extensive residence in the environment and their threat to public health. The contents of 16 l PAHs in air, particles, lake water and aquatic organisms were measured; physiological and behavior parameters influencing PAH exposure were collected; potential sources were identified; and cancer risks were calculated by US EPA model. The aims of this study were to elucidate the characteristics of multi-media PAH exposure of residents and to provide information for PAH management near Lake Chaohu.

## 2. Materials and Methods

### 2.1. Sample Collection and Pretreatment

Two sampling sites were selected near Chaohu City and Zhongmiao Town as urban and rural sites (Figure 1). Atmosphere samples were collected once a month from May 2010 to April 2011 by high-volume samplers. Polyurethane foam (PUF) disk and glass fiber filter (GFF) were used to collect gaseous phase and particulate phase PAHs, respectively. Water was collected from two sampling sites selected near the atmospheric sites. After shaking and mixing, a one liter aliquot of each collected water sample was filtered through a 0.45 µm glass fiber filter using a filtration device consisting of a peristaltic pump (80EL005, Millipore Co., Billerica, MA, USA). Edible aquatic organisms, including spotted steed (*Hemibarbus maculatus*, HM), carp (*Cyprinus carpio*, CC), snail (*Cipangopaludina chinensis* Gray, CCG), topmouth culter (*Culter erythropterus*, CE), bluntnose black bream (*Megalobrama amblycephala*, MA), Chinese white prawn (*Leander modestus* Heller, LMH), whitebait (*Hemisalanx prognathus* Regan, HPR) and bighead carp (*Aristichthys nobilis*, AN), were randomly collected in the lake.



**Figure 1.** The location of Lake Chaohu and sampling sites: (a) People's Republic of China, (b) Anhui Province and (c) Lake Chaohu.

In the laboratory, PUF and GFF samples were added with surrogate standards of 2-fluoro-1, 10-biphenyl and p-terphenyl-d14 (J&K Scientific, Beijing, China, 2.0 mg mL<sup>-1</sup>) before measurement. The PUF was Soxhlet extracted with 150 mL 1:1 mixture of n-hexane and acetone for 8 h. GFF was extracted by 25 mL hexane/acetone mixture (1:1) using a microwave accelerated reaction system (CEM Corporation, Matthews, NC, USA). Microwave power was set at 1200 W, and the temperature program was set to the following: ramp up to 100 °C in 10 min and held at 100 °C for another 10 min. Both PUF and GFF extracts were concentrated to 1 mL by rotary evaporation at a temperature below 38 °C and then transferred to a silica/alumina chromatography for cleanup. The elution solution was collected, concentrated, converted to hexane solution and then added with internal standards (Nap-d8, Ace-d10, Ant-d10, Chr-d12 and Perylene-d12, J&K Scientific Ltd., Beijing, China).

The water samples were extracted by using a solid phase extraction (SPE) system (Supelco, Bellefonte, PA, USA). C18 cartridges (500 mg, 6 mL, Supelco, Bellefonte, PA, USA) were prewashed with dichloromethane (DCM) and conditioned with methanol and de-ionized water. A 1 L water sample was added with surrogate standards, 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 in a water bath and was adjusted to a volume of 1 mL with hexane. Internal standards were added for analysis.

The fish samples were pretreated on the same day after being delivered back to the temporary laboratory. The muscles on both sides of the dorsal and chest were mixed. After obtaining the wet weight, the samples were freeze dried (FDU-830, Tokyo Rikakikai Co., Tokyo, Japan) and grounded into a granular powder with a ball mill (MM400, Retsch GmbH, Haan, Germany). Two gram powder samples were weighed into an extraction tube, and the surrogate standards were added to the samples to indicate recovery. After microwave extraction, the extracts were pressure filtered and concentrated to approximately 1 mL and cleansed by GPC instrument (GPC800+, Lab Tech Ltd., Hongkong, China) with a Bio Beads SX-3 column (300 mm × 20 mm, Bio-Rad Laboratories, Inc., Hercules, CA, USA). Subsequently the concentrate was loaded in a silica gel SPE cartridge (6 mL, 500 mg, Supelco Co., Bellefonte, PA, USA). The cartridge was eluted by hexane and mixed solution of dichloromethane and hexane. The extracts were concentrated to 1 mL, transferred to vials, added with internal standards and sealed for analysis. The details of experiment have been reported in previous research [19,26].

## 2.2. Instrument Analysis

The samples were analyzed by using Agilent 6890 gas chromatography and a 5976C mass spectrometer detector with a HP-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 µm).

Helium was used as the carrier gas at a flow of 1 mL/min. The samples (1 µL) were injected by the autosampler under a splitless mode at a temperature of 220 °C. The column temperature program was as follows: 50 °C for 2 min, 10 °C/min to 150 °C, 3 °C/min for 240 °C, 240 °C for 5 min, 10 °C/min for 300 °C and 300 °C for 5 min. The ion source temperature of the mass spectrometer was 200 °C, the temperature of the transfer line was 250 °C and the temperature of the quadrupole was 150 °C. The compounds were quantified in the selected ion mode, and the calibration curve was quantified with the internal standard. There were three parallel samples in each species. The method blanks and procedure blanks were prepared following the same procedure.

The quantification was performed by the internal standard method. All of the solvents used were HPLC-grade pure (J&K Chemical, Beijing, China). All of the glassware was cleaned by using an ultrasonic cleaner (KQ-500B, Kun Shan Ultrasonic Instruments Co., Ltd., 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 and sample blanks were analyzed with the true samples. A total of 16 priority control PAHs were measured. The PAH individuals, abbreviations as well as method recoveries in different environment media and aquatic organisms are shown in Table 1.

**Table 1.** Recoveries and toxicity equivalency factors (TEFs) of 16 PAHs.

Abbreviation	PAHs	Gaseous (%)	Particulate (%)	Water (%)	Aquatic Organisms (%)	TEF
Nap	Naphthalene	46	47	81	115	0.001
Acy	Acenaphthene;	51	48	87	101	0.001
Ace	Acenaphthylene	67	50	81	117	0.001
Flo	Fluorene	75	57	103	105	0.001
Phe	Phenanthrene	83	69	108	107	0.001
Ant	Anthracene	77	71	93	101	0.01
Fla	Fluoranthene	98	87	89	113	0.001
Pyr	Pyrene	124	88	89	122	0.001
BaA	Benzo[a]anthracene	99	97	63	102	0.1
Chr	Chrysene	92	102	62	119	0.01
BbF	Benzo[b]fluoranthene	121	103	43	105	0.1
BkF	Benzo[k]fluorant hene	90	111	44	102	0.1
BaP	Benzo[a]pyrene;	108	103	60	87	1
IcdP	Dibenz[a,h]anthracene	102	119	31	89	0.1
DahA	Indeno [1,2,3-cd]pyrene	127	118	24	93	1
BghiP	Benzo[ghi]perylene	65	115	24	110	0.01

### 2.3. Positive Matrix Factorization (PMF)

In this study, positive matrix factorization method was applied in order to quantitatively identify the major sources. PMF is a useful factorization methodology that can determine source profile and contribution [27,28]. The PMF model can be expressed as follows:

$$X = GF + E \quad (1)$$

where  $X$  is the concentration matrix, consisting of  $n$  samples and  $m$  concentrations of the compounds ( $n \times m$ );  $G$  is the factor contribution matrix;  $F$  is the factor profile matrix; and  $E$  ( $n \times m$ ) is the residual matrix. The elements of residual matrix are denoted as the following:

$$e_{ij} = x_{ij} - \sum_{k=1}^p g_{ik}f_{ki} \quad (2)$$

where  $x_{ij}$ ,  $f_{ki}$  and  $g_{ik}$  are the corresponding elements of  $X$ ,  $F$  and  $G$ , respectively. Non-negativity constraints are imposed on the contribution and profile matrices, and PMF

simultaneously weights individual data points based on uncertainty.  $Q(E)$  is an object function and a criterion for the model, defined as the following:

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m (e_{ij}/s_{ij})^2 \quad (3)$$

where  $s_{ij}$  is the uncertainty of the  $j$ th compound in the  $i$ th sample.

#### 2.4. Multi-Pathway Exposure and Risk Assessment

The BaP equivalent concentration ( $BaP_{eq}$ ) and toxicity equivalency factors (TEFs) were used to express the effects of exposure to mixtures of PAHs on health [29].  $BaP_{eq}$  is directly derived from the mass concentrations of different PAHs using TEFs. Therefore, they can be directly compared and contrasted [30]. In order to evaluate the total exposure to dietary PAHs,  $BaP_{eq}$  based on BaP toxicity was determined using the following equation:

$$BaP_{eq} = \sum C_i \times TEF \quad (4)$$

where  $C_i$  is the concentration of the PAH species in food, and  $TEF_i$  is the toxic equivalence factor of the PAH's congener  $i$ . (Table 1).

In accordance with the *Exposure Factors Handbook* [31], the lifetime average daily dose (LADD) of PAH exposure through inhalation (air and particle), aquatic product ingestion, and water intake was calculated as follows:

$$LADD = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (5)$$

where  $C$  is the concentration of PAHs in the environment media, and  $IR$  is the intake rate of PAHs through inhalation ( $IR_{inh}$ ,  $m^3 \cdot day^{-1}$ ), water intake rate ( $IR_{water}$ ,  $mL \cdot day^{-1}$ ) and aquatic product intake rate ( $IR_{inh}$ ,  $g \cdot day^{-1}$ ).  $EF$  is the exposure frequency ( $day \cdot year^{-1}$ );  $ED$  is the exposure duration (year); and  $BW$  is body weight (kg).  $AT$  is the average lifespan for carcinogens.

High uncertainty exists in risk assessment. Sample measurement errors were inevitable. There are also uncertainties in the parameters and estimates. In probabilistic risk assessment, exposure parameters are considered as random variables. In order to quantify experiment uncertainty and its impact on the estimation of expected risk, a 10,000 times Monte Carlo (MC) technique was used. The Crystal Ball software was employed to implement MC simulation.

### 3. Results and Discussions

#### 3.1. PAH Residual Levels in Environment Media

The levels of PAHs in the environmental media from Lake Chaohu are presented in Table 2. Sixteen priority PAHs were all detected during both the gaseous phase and particulate phase. In comparison, the detection rates of PAHs with higher than four rings in the water phase were very low due to their poor hydrophilic. The total concentrations of 16 priority PAHs ( $PAH_{16}$ ) in gaseous and particulate phases were  $59.4 \pm 51.4 \text{ ng} \cdot m^{-3}$  and  $14.2 \pm 23.5 \text{ ng} \cdot m^{-3}$ , respectively. The average gaseous  $PAH_{16}$  concentrations in urban and rural sites were 3.59 times and 4.95 times higher than in particles. The atmospheric  $PAH_{16}$  residual level in this study was lower than the values reported in Guangzhou ( $337 \text{ ng} \cdot m^{-3}$ ) [32] and in Tianjin ( $752 \text{ ng} \cdot m^{-3}$ ) [33], but it was greater than the highest level reported in mountain Taishan ( $9.07 \text{ ng} \cdot m^{-3}$ ) [34]. Compared with data reported abroad, the  $PAH_{16}$  level was higher than data reported in Chesapeake Bay ( $5.31 \sim 71.6 \text{ ng} \cdot m^{-3}$ ) [35], Athens ( $4.8 \sim 76 \text{ ng} \cdot m^{-3}$ ) [36] and in southwest Europe ( $0.32 \text{ ng} \cdot m^{-3}$ ) [37].  $PAH_{16}$  in the muscle of fish from Chaohu Lake (also including snail and shrimp) was also comparable with data reported from other freshwater fish in Hebei ( $4.76 \sim 144 \text{ ng/g}$ ) [20] and less than data reported in Shanxi ( $160 \text{ ng/g}$ ) [38]. Generally speaking, the  $PAH_{16}$  contents



in environment media and fish indicated a low PAH pollution level in Lake Chaohu. In order to compare the toxicity of difference environment media, the concentrations were converted to  $BaP_{eq}$  concentrations. Although the gaseous phase had much higher PAH<sub>16</sub> content, the  $BaP_{eq}$  was much higher in particles. The particulate  $BaP_{eq}$  in urban and rural were 11.2 and 5.51 times higher than those in the gaseous phase. The difference between PAH<sub>16</sub> and  $BaP_{eq}$  can be attributed to PAH composition in gas and particles.

**Table 2.** Residual levels of PAH<sub>16</sub> and  $BaP_{eq}$  in environmental media.

Categories	Media	Unit	Urban			Rural			Kruskal-Wallis Test
			Min	Max	GM	Min	Max	GM $\pm$ SD	
PAH <sub>16</sub>	Gas	ng·m <sup>-3</sup>	22.1	186	49.5 $\pm$ 46.0	10.9	183	72.3 $\pm$ 54.3	$p = 0.157$
	Particle	ng·m <sup>-3</sup>	3.41	82.5	13.8 $\pm$ 25.6	2.74	69.3	14.6 $\pm$ 22.4	$p = 0.773$
	Water	ng·L <sup>-1</sup>	57	409	171 $\pm$ 119	59.6	779	169 $\pm$ 188	$p = 0.544$
	Fish	ng·g <sup>-1</sup>	18.5	1029	114 $\pm$ 315	18.5	1029	114 $\pm$ 315	
$BaP_{eq}$	Gas	ng·m <sup>-3</sup>	0.04	0.38	0.14 $\pm$ 0.10	0.06	1.05	0.31 $\pm$ 0.26	$p = 0.010$
	Particle	ng·m <sup>-3</sup>	0.38	10.1	1.57 $\pm$ 2.99	0.31	9.00	1.71 $\pm$ 2.74	$p = 0.840$
	Water	ng·L <sup>-1</sup>	0.17	1.57	0.46 $\pm$ 0.42	0.26	1.36	0.54 $\pm$ 0.36	$p = 0.862$
	Fish	ng·g <sup>-1</sup>	0.29	20.2	1.75 $\pm$ 6.24	0.29	20.2	1.75 $\pm$ 6.24	

PAH<sub>16</sub>: The sum of 16 PAH components; GM: geometric mean; SD: standard deviation.

Spatial difference between urban and rural sites were compared by using the Kruskal–Wallis test. No significant difference was found between two sampling sites except gaseous  $BaP_{eq}$ . A  $p < 0.05$  significant difference was detected between urban and rural gaseous  $BaP_{eq}$  concentrations. The results showed that the concentrations in most environment media were similar in urban and rural area. There may be two reasons accounting for the small spatial difference. First, both Chaohu City and Zhongmiao Town had small populations. No obvious different lifestyle was found between people in urban and rural areas. In particular, there is no obvious heating season in the area around Chaohu. Thus, local emission sources in urban and rural area were not obvious. Second, the city and the town were far away from the local thermal power plant and other industrial pollution sources, resulting in low local pollution levels.

The PAH compositions in environment media were illustrated in Figure 2. It can be observed that the water phase was dominated by the low molecular PAHs. PAHs with less than three rings accounted for 95.0% and 93.3% of total PAHs in water. The same ratios in gaseous phase were 87.1% and 82.9% in urban and rural samples. In the particulate phase, however, the PAHs with more than or equal to four rings contributed to 80.2% and 81.6% of the total PAHs. The high proportion of high molecular weight PAHs results in the increase in toxicity due to the high TEF of high molecular weight PAHs.

Spearman's correlation analysis was used to detect the relationship between content of PAHs in gaseous, particulate phase, water and in aquatic animals. As a result, a significant positive correlation was found between gaseous phase and water phase (Figure 3a). It is reported that wet deposition, dry deposition and gas exchange across the air–water interface are the three major ways that PAHs can enter the water system. The result suggested that gas exchange across the air–water interface is probably an important way for atmospheric PAHs to affect the aquatic system [39]. In contrast, the relationship between particulate and dissolved PAHs was not significant ( $p = 0.116$ ). This can be partly explained by the solubility of different composition in particles and gas phase. The solubility of high molecular weight PAHs was lower than the solubility of those with low molecular weight. On the other hand, high molecular weight PAHs dominated the particle component. Thus, concentration levels of PAHs in particles had a weak correlation with their concentration levels in water. Significant positive correlation was also found between PAH in water and in fish tissues, which indicates the effect of environmental concentration on organisms.

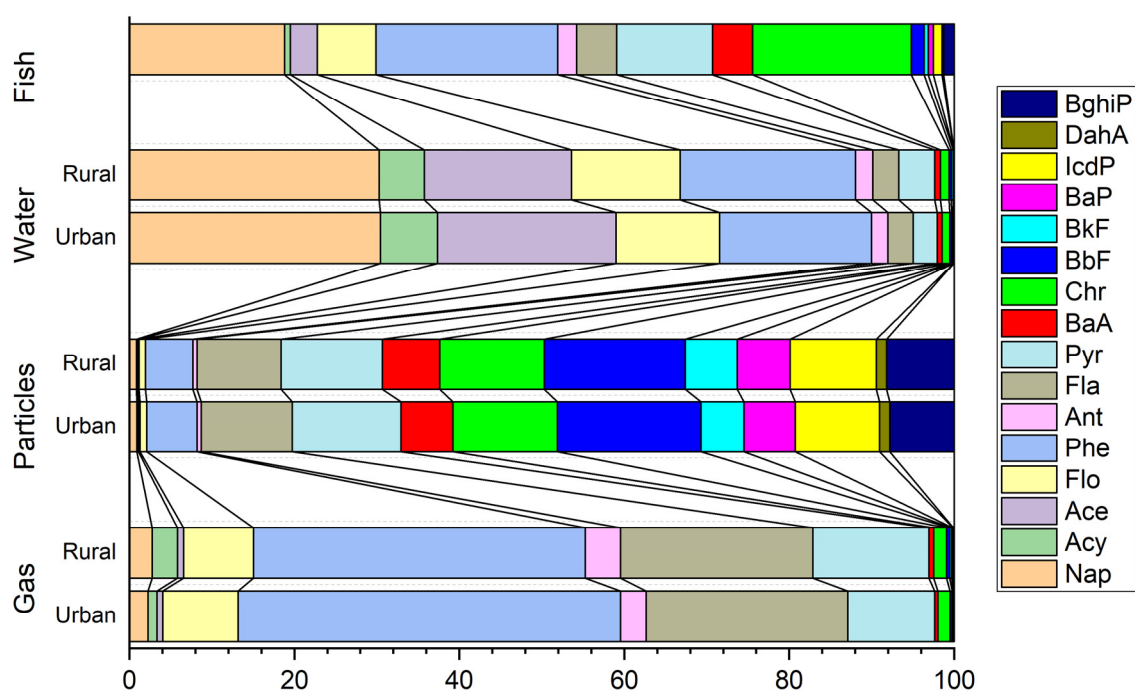


Figure 2. PAHs composition in different environment media.

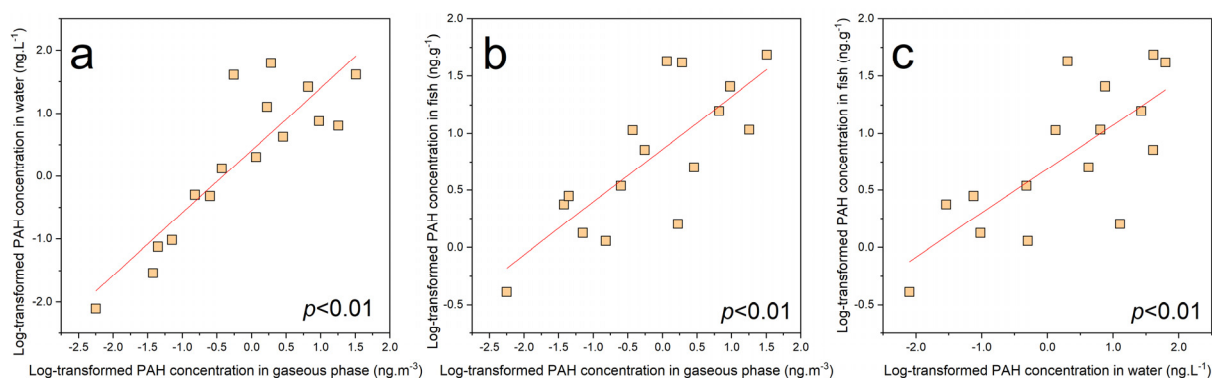


Figure 3. Spearman correlation between PAH levels in environment media (a) water and gaseous phase (b) and fish tissues and gaseous phase (c) water and fish tissues.

### 3.2. Source Apportionment

#### 3.2.1. Molecular Diagnostic Ratios

PAHs can be formed by multiple anthropogenic activities such as combustion of fossil fuels, or they can be formed naturally in the environment by oil seeps and plant debris and forest and prairie fires. Some methods have been established in order to identify PAH sources: for example, molecular diagnostic ratios (MDRs), the principal component analysis (PCA) method [37,40], the chemical material balance (CMB) model [41], the positive matrix factorization (PMF) method and stable carbon isotopic ratios analysis [42]. In this study, MDRs and PMF were used to identify the major sources and to obtain a reliable conclusion.

The MDR theory [17,43] is based on the hypothesis that some PAH ratios remain constant between the source and the receptor. The MDR method has been widely used in the identification of preliminary sources [44]. Based on the monitoring data, four normally used ratios were employed in this research. Common ratios used include Ant/(Ant + Phe) (mass 178), Fla/(Fla + Pyr) (mass 202), BaA/(BaA + Chr) (mass 228) and IcdP/(IcdP + BghiP) (mass 276).

The ratios of mass 178 increased from January and reached the peak in October (Figure 4). Generally, the ratios varied near the value of 0.1. The lowest value was obtained during the winter, and the highest value was achieved in the summer. For mass 178, a ratio  $< 0.10$  usually is taken as an indication of petroleum, whereas a ratio  $> 0.10$  indicates a dominance of combustion. From November to January, petroleum was the dominant source, and emission from combustion became the greatest contributor during the rest of the year. For mass 202, a ratio of 0.50 is usually defined as the petroleum/combustion transition, and point ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel (vehicle and crude oil) combustion, whereas ratios  $> 0.50$  are characteristic of grass, wood or coal combustion. The ratios in our study indicated a strong influence of biomass and coal combustion before November, which was consistent with the result of mass 178. For mass 228, BaA/(BaA + Chr), ratios  $< 0.20$  indicate petroleum sources, ratios from 0.20 to 0.35 indicate either petroleum or combustion and those  $> 0.35$  imply combustion. The ratios from May to October were higher than 0.5, which indicated grass, wood or coal combustion. From November to April, the ratios were between 0.40 and 0.50, which was the characteristic of liquid fossil fuel combustion. For IcdP/(IcdP + BghiP), ratios  $< 0.20$  likely indicates petroleum, those between 0.20 and 0.50 imply liquid fossil fuel combustion and ratios  $> 0.50$  imply grass, wood and coal combustion. The ratios of mass 228 in our research indicated a mixture of petroleum or combustion. Combustion was the potential source from July to December. The ratios in our research suggested a potential combustion source [45].

The MDRs indicated that PAHs in Lake Chaohu were mainly from combustion and vehicle emission. We can also found that differences existed when we were using different PAH ratios. The use of PAH MDRs has been criticized in the past due to low accuracy. Overlap areas were reported between commonly applied ratios associated with different types of PAH emissions [44,46]. According to a study of MDRs based on the inventory and monitoring data over 20 years, it was found that the use of MDRs does not respond to known differences in atmospheric emission sources unless the source is strong [47]. due to the limitations of MDRs, a PMF model was also applied to detect the potential sources.

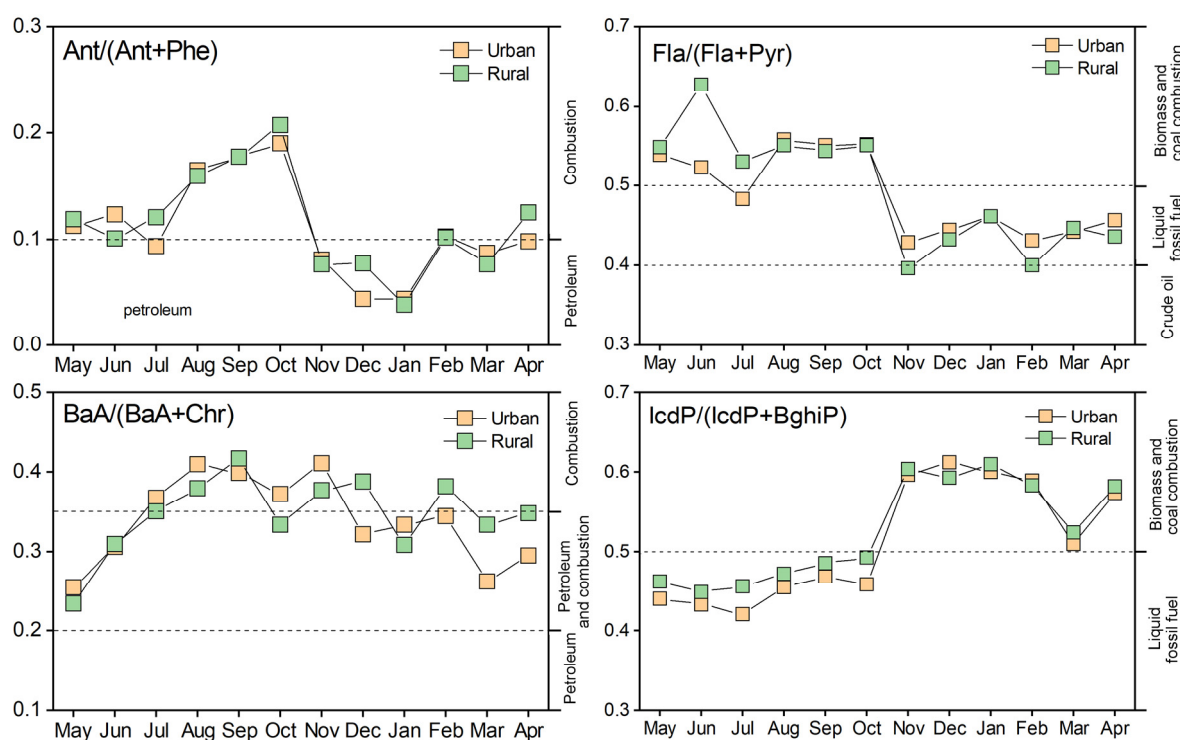


Figure 4. Seasonal and spatial variation of four ratios in atmospheric samples from Lake Chaohu.



### 3.2.2. PMF Results

When the number of factors for PMF is three, good simulation has been achieved for most PAHs. Therefore, three components were extracted, and the source profiles of three factors are illustrated in Figure 5. It was found that factor one is predominately weighted by low molecular weight PAHs. Factor two is heavily weighted by the middle molecular weight PAHs, and factor three has a higher contribution in the PAHs with more than four rings. The first factor is predominately weighted by Acy, which has been proved to be a tracer of combustion of straws. In addition, factor one has high load on Fla, Pyr and Chr, which are the combustion products of firewood. Therefore, factor one appears to be biomass combustion. Factor two is predominately weighted by Phe and BbF. According to the literature, Flo, Phe and Ant are predominantly considered as coal combustion profiles. The high BbkF and Chr loads are also a typical sign of Chinese domestic coal emissions [2,17,48,49]. Factor two is supposed to be coal combustion emission. For factor three, BghiP has been identified as tracers of auto emissions, and IcdP is considered as a marker of diesel emission. It can be concluded that factor three represents emission from vehicle.

The percentages of the sources from the factors were estimated by PMF. These results showed that the sources from biomass combustions, coal combustion and vehicle emission accounted for 43.6%, 30.6% and 25.8% of the total PAHs, respectively. Compared with the result of MDRs, a similar conclusion was obtained by PMF and MRDs. It can also be observed that coal combustion plays an important part in local PAH emission. Our conclusion is different from some research studies conducted in China. Most domestic studies show that coal is the main source of pollution in China, which is related to the fact that coal is the main energy material in China. China is the largest coal producer and consumer in the world [50]. According to the National Bureau of Statistics, the coal production of China in 2018 was 3.5 billion tons, nearly half of the world's production. Thus, the high coal consumption produces high PAH contribution to the atmosphere. In this study, the atmospheric samples were collected from Mushan island and Chaohu City. The former is a rural area far away from the city, while the latter is a small city with a small population and is a suburb surrounded by rural areas. Compared with coal combustion, firewood combustion is a more important method supplying energy in the research area.

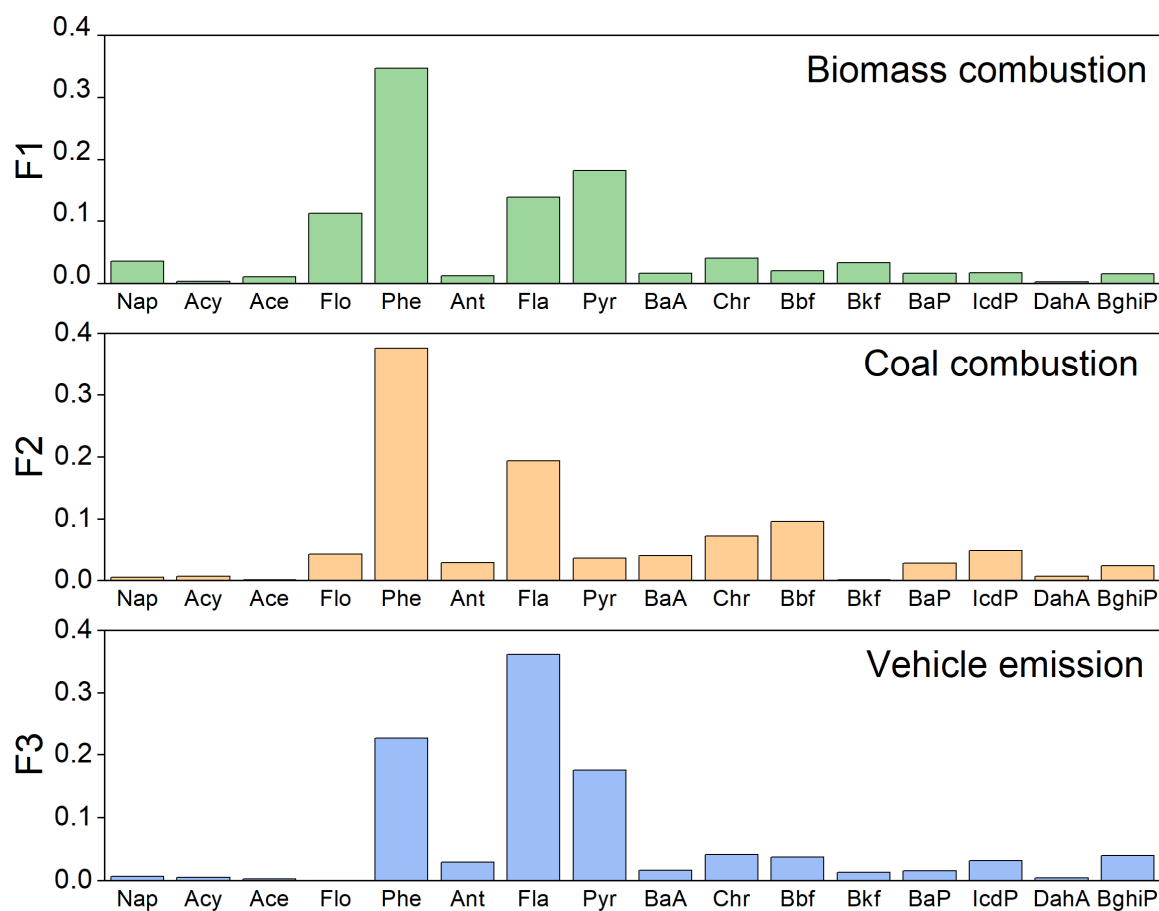
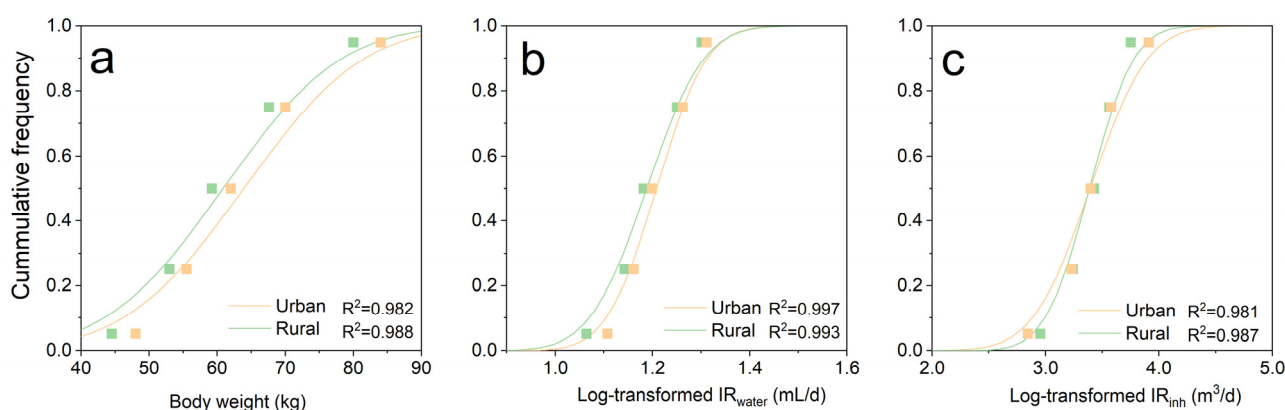


Figure 5. Factors of PMF analysis in Chaohu dustfall.

### 3.3. Exposure through Different Pathways

#### 3.3.1. Derivation of Exposure Parameters

Three physiological and exposure behavior parameters including bodyweight, water intake rate and inhalation rate were collected from *Exposure Factors Handbook of Chinese Population* [51]. The distribution modes of parameters were fitted by regression models. Specifically, first, we considered a normal distribution for BW and log-normal distributions for the water intake rate and inhalation rate because the normal and log-normal distribution models are the most widely applied in studies on the exposure parameters [52,53]. Second, the 5th, 25th, 50th, 75th and 95th percentiles were collected from the *Exposure Factors Handbook*. The distribution of the parameters was fitted using the Gaussian function. The fit curves and parameters are shown in Figure 6 and Table 3, respectively. It can be observed that relatively good regression results were obtained for all three parameters. In addition, the intake rates of fish consumption in urban and rural were considered as constants. According to a survey conducted between 2010 and 2013, the average daily intakes of freshwater products per capita were 19.0 g/day and 11.1 g/day for the urban and rural populations, respectively [54].



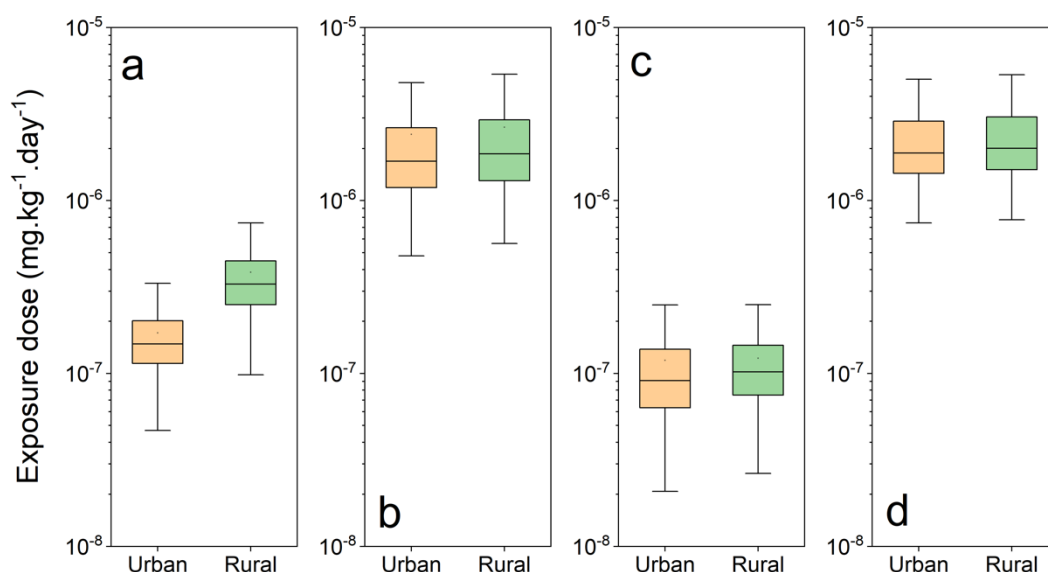
**Figure 6.** Fitting of (a) bodyweight, (b) water intake rate and (c) inhalation rate of urban and rural population in Anhui Province.

**Table 3.** Exposure parameters of adults for Monte Carlo simulation.

Media	Unit	Distribution Mode	Urban	Rural	References
Water	ng·L	Log-Normal	LN(−0.77, 0.68)	LN(−0.62, 0.56)	Measured
Gas	ng·m <sup>−3</sup>	Log-Normal	LN(−1.96, 0.67)	LN(−1.18, 0.71)	Measured
Particle	ng·m <sup>−3</sup>	Log-Normal	LN(0.45, 1.10)	LN(0.54, 1.11)	Measured
Fish	ng·g <sup>−3</sup>	Log-Normal	LN(0.56, 1.48)	LN(0.56, 1.48)	Measured
BW	Kg	Normal	N(63.90, 13.86)	LN(60.86, 13.64)	[53]
IR(water)	mL·d <sup>−3</sup>	Log-Normal	LN(7.81, 0.91)	LN(7.80, 0.70)	[53]
IR(inh)	m <sup>3</sup> ·d <sup>−1</sup>	Log-Normal	LN(2.78, 0.19)	LN(2.74, 0.21)	[53]
IR(fish)	g·d <sup>−3</sup>	Constant	19.0	11.1	[54]

### 3.3.2. Estimation of Exposure Doses

The lifetime average daily doses (LADD) of  $BaP_{eq}$  exposure through inhalation (air and particle), aquatic product ingestion and water intake were calculated by 10,000 iterations of Monte Carlo simulation. The results were illustrated in Figure 7.  $BaP_{eq}$  exposure through fish ingestion had the greatest contribution, with the average value of  $3.01 \times 10^{-6}$  ( $\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$ ). The LADD of residents in urban and rural were  $2.97 \times 10^{-6}$  ( $\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$ ) and  $3.07 \times 10^{-6}$  ( $\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$ ), respectively. Although the fish intake rate in urban residents was 1.71 times higher than that in rural, no obvious difference was observed between two population groups. Exposure through particle inhalation has a comparable contribution of  $2.54 \times 10^{-6}$  ( $\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$ ), which is one and two order of magnitude higher than exposure through gas inhalation and water ingestion, respectively. Our results are consistent with previous research. It has been reported that, for most non-occupationally exposed individuals, diet is the main route of exposure [55,56]. Inhalation of gaseous and particulate also had an ignorable contribution relative to the total  $BaP_{eq}$  exposure.

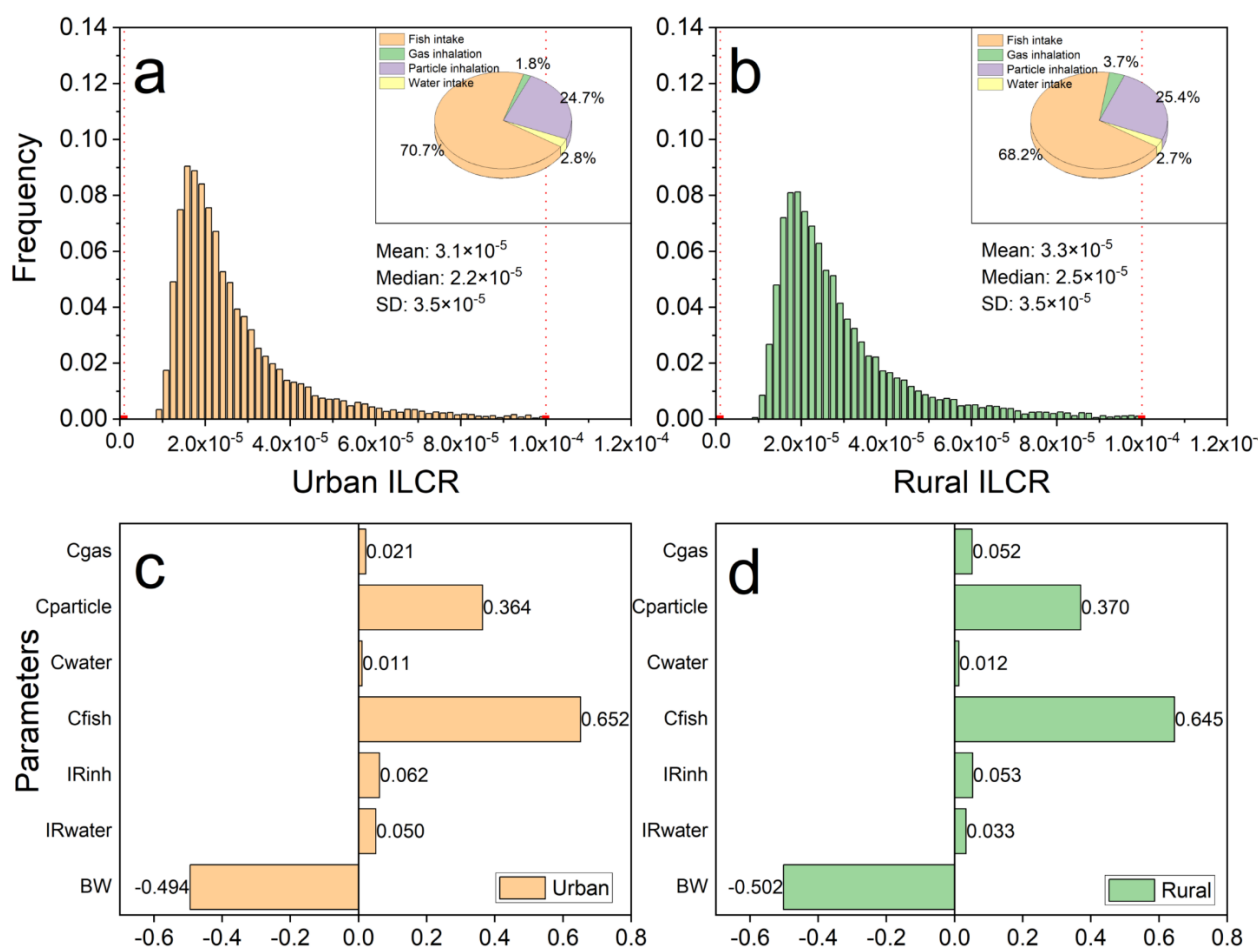


**Figure 7.**  $BaP_{eq}$  exposure through different pathways: (a) gaseous phase; (b) particulate phase; (c) water intake; and (d) fish intake.

### 3.4. Carcinogenic Risk Assessment

The probabilistic cancer risk for urban and rural residents were obtained based on the results of Monte Carlo simulation and presented in Figure 8a,b. The median total PAHs ILCR was  $3.1 \times 10^{-5}$  to  $3.3 \times 10^{-5}$  in urban and rural residents, which showed a slightly higher carcinogenic risk for rural residents than that for urban residents. The difference can be attributed to the variation of exposure behaviors. A one in a million chance of additional human cancer over a 70-year lifetime ( $ILCR = 10^{-6}$ ) is considered acceptable or inconsequential, and one in ten thousand or greater ( $ILCR = 10^{-4}$ ) is considered serious (US EPA). Most of the surrogate samples generated by Monte Carlo distributed between the range of  $10^{-6}$  and  $10^{-4}$ , which indicates potential ILCR risk. Due to the different end points, the carcinogenic slopes of inhalation and ingestion are quite different. Therefore, fish ingestion had much higher contribution than particle inhalation. Inhalation (including gas and particles) accounted for 26.5% and 29.1% of the total risk in urban and rural areas, respectively.

Parameter sensitivity was quantitatively assessed by the Spearman's rank correlation coefficient of parameter and risk. The result was shown in Figure 8c,d. As the dominant exposure pathway, fish consumption had the highest risk contribution. PAH concentration in fish had the highest influence on the results of risk assessment. As the most important protection factor, the bodyweight was the second most sensitive parameter. PAH concentration associated with particles was the third most sensitive parameter in this research. It can also be observed that the sensitivity of exposure behavior parameters were relative low compared with media concentrations. This can be attributed to the small difference of these parameters among adults. As the most important behavior parameter, fish consumption rate was not treated as variables in the study due to the limited data support. However, the uncertainty of intake rate of fish should not be ignored due to the high contribution of fish intake on the total risk, which requires further research and more data support in the future.



**Figure 8.** Distributions of incremental lifetime cancer risk (a,b) and parameter sensitivity for urban and rural populations (c,d) derived using the Monte Carlo simulation.

#### 4. Conclusions

PAHs in major environment samples were collected in Lake Chao for the entire year. Exposures through four pathways were estimated. ILCRs were characterized. The results found that the gaseous concentration had influence on the PAHs in the water according to the Spearman correlation analysis and may further affect the PAH content in fish tissues. Atmospheric transport is the source of the entire water system. The results of sources apportionment on atmospheric samples indicated the high contribution of biomass combustion. Probabilistic risk assessment suggested that inhalation and fish ingestion are two major pathways of PAH exposure, which are also the key processes in PAHs' risk control for people near Lake Chaohu.

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