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Residual levels and health risk of polycyclic aromatic hydrocarbons in freshwater fishes from Lake Small Bai-Yang-Dian, Northern China

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ABSTRACT

The residual levels of polycyclic aromatic hydrocarbons (PAHs) in the liver, brain, gill and muscle tissues of four common edible freshwater fish species including crucian carp, snakehead fish, grass carp and silver carp collected from Lake Small Bai-Yang-Dian in northern China were measured by GC–MS. The distribution and composition pattern of PAHs in the fish tissues, and the effects of lipid contents in fish tissues and the octanol–water partition coefficient (Kow) of PAHs congeners on them were analyzed. The human health risk of PAHs though fish consumptions was estimated. The following results were obtained: (1) The average residual levels of total PAHs (PAH_{16}) on wet weight base in the different tissues of each fish species ranged from 4.764 to 144.254 ng/g ww. The differences in the average residual levels on wet weight base for PAH_{16} within four fish species were not statistically significant ($P > 0.05$); however, these within four fish tissues were statistically significant ($P < 0.01$). (2) There were very similar distribution patterns of PAH congeners among both the fish tissues and the fish species, as indicated by statistically significant positive interrelationships ($R = 0.58–0.97$, $P < 0.01$ or $P < 0.05$). Low molecular weight (LMW) PAHs predominated the distribution in the fish tissues, accounting for 89.97% of total PAHs. Phe was the most dominant component, according for 37.79% of total PAHs, followed by Ant (18.59%), Flo (12.59%), Nap (10.79%), Fla (9.82%) and Pyr (6.43%). (3) The PAHs residues and distribution in the fish tissues are dependent on both the Kow of PAH congeners and the lipid contents in the fish tissues. There was a significant positive relationship ($R = 0.7116$, $P < 0.0001$) between lipid contents and PAHs residual levels. The statistically significant negative relationships ($P < 0.05$) were found between LogKow and log-transformed PAHs contents on wet weight base for all fish tissues except for the muscle tissue of snakehead fish, the brain and liver tissues of crucian carp. (4) The risk levels of total PAHs were lower than 10^{-5} for the muscle tissues of four studied fish species and for the brain tissues of grass carp and snakehead fish; while these were higher than 10^{-5} for the brain tissues of crucian carp and silver carp. The risk levels of total PAHs in the liver tissues of four studied fish species except for snakehead fish exceeded 10^{-5} for 2–4.5 times. However, the potency equivalent concentration (PEC) of total PAHs in four studied fish tissues were still lower than the maximum permissible BaP limits for crops and baked meat and for plants in the national criterions. The distributions of PAH congeners in fish were well simulated by a level III fugacity model, especially for low molecule weight PAHs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group complex mixture with more than 10,000 individual compounds having two or more fused benzene rings (Dennis, 2007). During last decades, due to their widespread occurrence, strong persistence, long-range transportation potential, and carcinogenic toxicity, much attention to their sources, distribution, transport, fate, toxicology and pollution-control countermeasures have been paid by many researchers, various academic institutions and international organizations (e.g. Keith and Telliard, 1979; Neff, 1979, 1985; Bouloubassi and Saliot, 1991; Shaw and Connell, 1994; Wagrowski and Hites, 1997; UNECE, 1998; Smith et al., 2001; UNEP, 2002; Tao et al., 2004, 2006; Dennis, 2007). The primary sources of PAHs are mainly from the incomplete combustion of various organic matters such as fossil fuels (e.g. coal, gasoline and diesel) and biomass fuels (e.g. straw, firewood) (Neff, 1979; Baek et al., 1991; Xu et al., 2006; Zhang and Tao, 2009). In many developed counties, the PAHs emissions have significantly decreased because of the improved efficiency of energy utilization in the past decades (Pacyna et al., 2003; Sun et al., 2006). However, in China, the PAH emissions have been increasing greatly due to the increasing energy demand associated with rapid population growth and economic development, and to the low efficiency of energy utilization (Xu et al., 2006; Zhang

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et al., 2007). In 2004, the atmospheric PAH emissions of 16 priority PAHs in China was estimated as 114 Gg, accounting for about 22% of the total global emission (520 Gg) of 16 priority PAHs set by USEPA (Zhang and Tao, 2009). The threaten of PAHs pollution to ecosystem and human health have became more and more serious in China.

Because of their importance in aquatic ecosystems and in human food sources, fishes are frequently used as the standardized testing protocols for such purposes as predicting the bioconcentration factor (BCF) (Barron, 1990), analyzing the bioaccumulation in organisms via the food chain (Haruhiko et al., 2003; Guo et al., 2008), evaluating the human health risk (Dong et al., 2006; Cheung et al., 2007; Dennis, 2007), and monitoring POPs pollution (Lanfranchi et al., 2006; Guo et al., 2008). Some studies on the occurrence of PAHs in different fish species were reported during last decades (e.g. Douabul et al., 1987; Eggens and Vethaak, 1989; Hontela et al., 1992; Tuvikene, 1995; Escartin and Porte, 1999; Pointet and Milliet, 2000; White & Triplett, 2002; Barron et al., 2004; Kong et al., 2005; Liang et al., 2007; Ackerman et al., 2008). However, distributions of PAHs in different fish tissues are still not well documented. Most of these studies only analyzed PAHs in fish muscles. PAHs distributions in other tissues, such as fish brain, liver and gill tissues have not been fully investigated. The distributions of PAHs in fish tissues other then mussels could provide more clues about the bioaccumulation and metabolism of PAHs in fishes. The residues of PAHs in such edible tissues as fish brain could also provide more information on the risk levels of PAHs to human health though fish consumptions.

Some investigations in china have been carried out on the PAHs pollution status of fresh waters, such as the Pearl River (Mai et al., 2002), the Yellow River (Li et al., 2006), and the Yangtze River (Feng et al., 2007). Lake Bai-Yang-Dian, the largest freshwater lake in Northern China, is located at the central place of three big cities, Beijing, Tianjing and Shijiazhuang, one of the most serious PAHs-polluted areas in China. The lake with total area of 366 km^2 is composed of 134 interknitted small lakes with different area. It is one of the important bases of fish production in China. However, during the last decades, with the rapid economic development and population growth in the watershed and neighbor regions, the lake receives the considerable increasing load of PAHs. The objectives of the present research are: (1) to investigate the residue levels of PAHs in the freshwater fishes from Lake Small Bai-Yang-Dian, with the area of 13.3 km^2, the biggest one among 134 interknitted small lakes in Lake Bai-Yang-Dian; (2) to explore the relationships between the residue levels of PAHs in freshwater fishes and the lipid contents in fish tissues as well as the octanol–water partition coefficient (Kow) of PAH congeners; and (3) to estimate the risk levels of PAHs to human health though the consumptions of freshwater fishes from the Little Bai-Yang-Dian Lake.

2. Materials and methods

2.1. Sample collection

In October 2007, four species of commonly consumed freshwater fishes, including 15 individuals of crucian carp (*Carassius auratus*), and 10 individuals of snakehead fish (*Channa argus*), grass carp (*Ctenopharyngodon idellus*), and silver fish (*Hypophthalmichthysmolitrix*), respectively, were collected from Lake Small Bai-Yang-Dian. Four fish tissues including brain, lever, gill and muscle (mixture of muscle from dorsal and chest) were sampled. In order to eliminate individual diversity, the specific tissues from 3 to 5 individuals of the same fish species were mixed as one sample. All fish samples were freeze-dried for 3–4 days after weighing, and then preserved in the dryer prior to analyses.

2.2. Sample extraction and cleanup

The freeze-dried fish tissue samples weighting 1–3 g were pulverized to pass through a 40-mesh sieve. The samples were Soxhlet extracted with 100 ml mixed solvent of dichloromethane and *n*-hexane (v:v, 1:1) for 24 h at 50 °C. Prior to extraction, the indicators of PAHs recovery including NAP-d8, ACE-d10, ANT-d10, CHR-d12 and Perylene-d12 were added to the samples. The extract was subjected to hexane-saturated acetonitrile to remove lipid through liquid–liquid extraction following by Haruhiko's procedure (Haruhiko et al., 2003). The extract was added to a separatory

Table 1
Residual levels[a] of PAHs on wet weight basis (ng/g ww) in the different tissues of each fish species.

PAH[b]	Grass carp				Snakehead fish			Crucian carp				Silver carp			
	Muscle	Brain	Gill	Liver	Muscle	Brain	Gill	Muscle	Brain	Gill	Liver	Muscle	Brain	Gill	Liver
Nap	2.307	5.756	2.401	1.215	0.888	3.618	2.316	1.730	3.422	2.311	0.305	1.272	4.211	1.152	5.611
Acy	0.210	1.566	0.766	0.492	0.304	1.372	0.283	0.220	1.578	0.273	0.792	0.184	0.452	0.154	0.571
Ace	0.136	0.337	0.317	0.240	0.131	0.500	0.097	0.135	0.397	0.127	0.338	0.167	2.077	0.055	0.094
Flo	0.969	5.563	4.375	3.085	2.646	5.326	0.670	13.573	6.683	0.728	4.799	1.262	6.599	0.442	2.697
Phe	13.547	105.892	10.616	4.854	1.684	13.538	10.603	35.125	25.866	2.726	9.911	3.096	44.777	1.472	3.253
Ant	8.361	16.982	1.663	3.364	1.404	4.413	18.346	0.771	0.664	–	1.611	7.608	33.967	0.739	0.210
Fla	0.764	3.944	2.354	5.240	–	4.217	0.436	0.135	5.564	0.323	5.007	0.677	3.109	0.302	4.889
Pyr	1.551	3.563	3.293	1.050	0.401	2.321	0.657	10.572	2.821	0.382	3.481	0.171	0.791	0.375	1.781
BaA	0.029	0.075	0.617	0.177	0.020	0.381	0.033	0.015	0.063	0.044	0.572	0.003	0.396	0.010	0.104
Chr	0.097	0.576	2.321	0.199	0.007	0.875	0.095	0.053	0.205	0.116	0.207	0.048	1.356	0.035	0.196
BbF	0.047	–[c]	0.294	0.207	0.018	0.095	0.039	0.038	–	0.091	0.601	0.034	0.268	0.002	0.083
BkF	0.012	–	0.109	0.055	–	0.039	0.009	0.009	–	0.025	0.180	0.004	0.000	0.002	0.128
Bap	–	–	0.243	0.071	–	0.151	0.004	0.003	0.129	0.020	0.275	–	0.198	–	0.181
IcdP	–	–	0.262	–	–	–	–	–	–	0.044	0.261	–	0.212	–	–
DahA	–	–	0.039	0.229	–	–	0.046	–	0.106	0.155	0.511	–	–	0.007	0.226
BghiP	–	–	0.035	0.092	–	–	0.045	–	–	0.110	0.349	0.009	–	0.016	0.097
LMW-PAHs	26.296	140.041	22.492	18.491	7.057	32.983	32.750	51.689	44.173	6.490	22.762	14.266	95.191	4.317	17.326
MMW-PAHs	1.735	4.214	6.633	1.687	0.446	3.712	0.834	10.686	3.089	0.658	5.041	0.261	2.812	0.424	2.292
HMW-PAHs	–	–	0.578	0.392	–	0.151	0.095	0.003	0.235	0.329	1.396	0.009	0.410	0.023	0.503
PAH_{16}	28.031	144.254	29.703	20.570	7.503	36.846	33.678	62.379	47.497	7.477	29.200	14.536	98.412	4.764	20.121

[a] Levels of PAHs are presented as mean ± standard deviation.

[b] Nap: naphthalene; Acy: acenaphthylene; Ace: acenaphthene; Flo: fluorene; Phe: phenanthrene; Ant: anthracene; Fla: fluoranthene; Pyr: pyrene; BaA: benzo[*a*]anthracene; Chr: chrysene; BbF: benzo[*b*]fluoranthene; BkF: benzo[*k*]fluoranthene; Bap: benzo[*a*]pyrene; IcdP: indeno[1,2,3-*cd*]pyrene; DahA: dibenz[*a*,*h*]anthracene; BghiP: benzo[*ghi*]perylene; PAH_{16}: the sum of 16 PAH components; LMW-PAH: low molecular weight PAHs including 2–3 ring PAHs (Nap, Acy, Ace, Flo, Phe, Ant, Fla); MMW-PAH: moderate molecular weight PAHs including 4 ring PAHs (Pyr, Baa, Chr, Bbf, Bkf); HMW-PAH: high molecular weight PAHs including 5-6 ring PAHs (Bap, Icdp, Daha, Bghip).

[c] "–" means below the detection limits.

funnel containing 50 ml of hexane-saturated acetonitrile and 20 ml of hexane. After extraction the acetonitrile was collected. This procedure was repeated till totally 100 ml of hexane-saturated acetonitrile was collected. And lipid content was extracted in hexane, which was determined by quality-subtraction method (Haruhiko et al., 2003).

A silica gel column was used for sample cleanup. A glass column (10 mm i.d. × 350 mm length) was first filled with 10 ml dichloromethane then packed with 10 g of silica gel (pre-soaked in dichloromethane), and approximately 20 mm length of anhydrous sodium sulfate. The extra dichloromethane was released while keeping the silica gel and the anhydrous sodium sulfate soaked. The columns were pre-eluted with 40 ml of pentane prior to use. The cleanup column was eluted with 25 ml of *n*-hexane followed by 50 ml of a 3:2 mixture of *n*-hexane and dichloromethane at a rate of 2 ml/min. The eluate collected from the silica column during cleanup was concentrated to 1 ml by the vacuum rotary evaporator. The internal standard compounds including 2-fluoro-1,1′-biphenyl, *p*-terphenyl-d14 were spiked to sample solution. The samples were sealed in vials and stored at −4 °C before analysis.

A mixed stock standard with 16 priority PAHs (PAH-Mixture, 610/525/550) was obtained from the Chem. Service Co. All solvents used for sample processing and analysis (dichloromethane, acetone, hexane petroleum ether, cyclohexane, methanol) were HPLC grade. Anhydrous sodium sulfate was of analytical grade and was activated at 450 °C to remove impurities before using.

Table 2
ANOVA results for the wet weight-based PAHs contents in fish species and tissues.

PAHs	Source of variation	Mean square	*F* value	*P* value
PAH_{16}	Fish species	3068.235	1.041	0.386**
	Fish tissues	14650.675	4.969	0.005*
LMW-PAHs	Fish species	2531.734	0.951	0.426**
	Fish tissues	14558.183	5.466	0.003*
MMW-PAHs	Fish species	33.531	0.814	0.495**
	Fish tissues	7.152	0.174	0.914**
HMW-PAHs	Fish species	0.136	1.137	0.347**
	Fish tissues	0.806	6.735	0.001*

The meanings for LMW-PAHs, MMW-PAHs and HMW-PAHs refer to Table 1.
* Significant difference at the significance level of 0.01 ($P < 0.01$).
** No significant difference ($P > 0.05$).

2.3. Sample analysis

16 priority PAHs identified by the USEPA including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), chrysene (Chy), benzo[*a*]anthracene

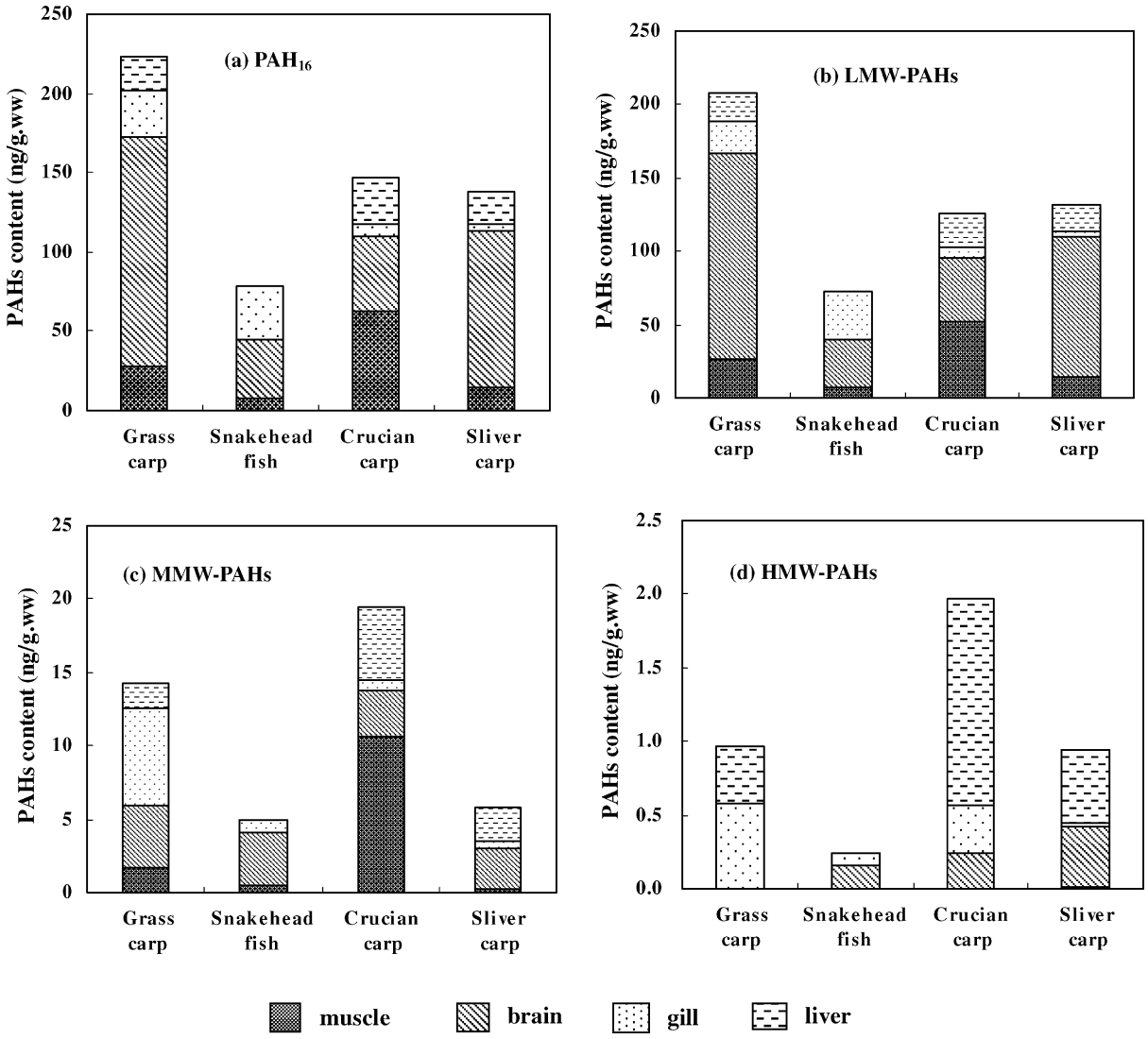

Fig. 1. Average wet weight contents of total PAHs (PAH16) (a), LMW-PAHs (b), MMW-PAHs (c) and HMW-PAHs (d) in four fish species from Lake Small Bai-Yang-Dian.

(BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IcdP), benzo[*ghi*]perylene (BghiP), dibenz[*a*,*h*]anthracene (DahA) were analyzed in this study. The analysis was conducted using an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer and a 7683 autosampler (Agilent Technology). A HP-5MS capillary column with 30 m × 0.25 mm i.d. × 0.25 mm film thickness was used. GC temperature was programmed from an initial 60 °C at 5 °C/min up to 300 °C, with a final holding time of 20 min. Helium was used as the carrier gas. A 1.0 μl aliquot of the extract was injected while the injector port was held at 300 °C and operated in splitless mode at a flow rate of 1.0 ml/min. The head column pressure was 30 kPa. The mass spectrometer was operated in scan mode with an electron impact ionization of 70 eV, an electron multiplier voltage of 1288 V, and an ion source 230 °C.

2.4. Quality control

Prior to the sample analysis, a mixed stock standard with 16 PAHs (PAH-Mixture, 610/525/550, Chem. Service Co.) was used to make the standard curve with the concentration of 1 ppb, 10 ppb, 100 ppb, 1000 ppb. The procedural blank was determined by going through the extraction and cleanup procedures using glass beads instead of fish samples. Recoveries of PAHs were determined by spiking fish samples with standards at both higher and lower concentrations. Recovery of individual PAHs ranged from 43.9% to 133.2% with a mean value of 92.3% for the 16 PAHs. All samples were extracted and analyzed in triplicate.

2.5. Data processing

The Shapiro–Wilk tests (sample size: $3 < n < 50$) was used to estimate data normality. A log-transformation was performed to ensure the normality distribution of the data in all fish tissues. A "one way analysis of variance (ANOVA)" was done to detect differences in data among the fish tissues and the fish species. The relationship between the data was determined by Pearson's sample correlation, and when the value of *P* was below 0.05, the linear regression was regarded as significant. The software used was SPSS 10.0 (SPSS Inc., Chicago, IL).

3. Results and discussions

3.1. PAHs residual levels

The residual levels of PAHs on wet weight basis in the different tissues of each fish species are tabulated in Table 1. ANOVA results within the fish species are shown in Table 2. The average wet weight contents of total PAHs (PAH_{16}), LMW-PAHs, MMW-PAHs and HMW-PAHs in four fish species and in the four fish tissues are presented in Figs. 1 and 2, respectively.

Table 1 shows that the average residual levels of PAH_{16} on wet weight base in the different tissues of each fish species ranged from 4.764 to 144.254 ng/g ww. The residual levels for PAH_{16} in the fish tissues exhibited the following order from high to low values: brain (144.254 ng/g ww) > gill (29.703 ng/g ww) > muscle (28.031 ng/g ww) > liver (20.57 ng/g ww) for grass carp, brain (36.846 ng/g ww) > gill (33.678 ng/g ww) > muscle (7.503 ng/g ww) for snakehead fish, muscle (62.379 ng/g ww) > brain (47.797 ng/g ww) > liver (29.2 ng/g ww) > gill (7.477 ng/g ww) for crucian carp, and brain (98.412 ng/g ww) > liver (20.121 ng/g ww) > muscle (14.536 ng/g ww) > gill (4.764 ng/g ww) for silver carp, respectively. The LMW-PAHs's residual levels followed the same trends as the PAH_{16}'s in the tissues of snakehead fish, crucian carp and silver carp with the exception of the muscle and gill tissues of grass carp. The average HMW-PAHs residual levels were highest in the liver tissues; and those in the muscle tissues ranged from below detection limits in grass carp and snakehead fish to 0.009 ng/g ww in silver carp.

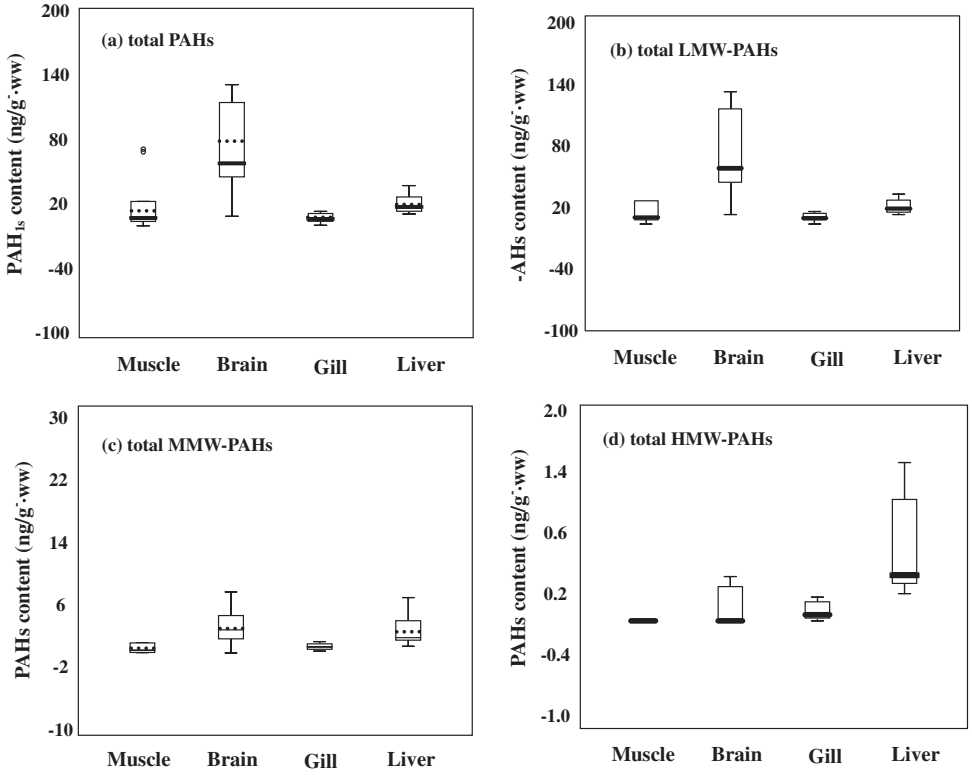

Fig. 2. Wet weight contents of total PAHs (PAH_{16}) (a), LMW-PAHs (b), MMW-PAHs (c) and HMW-PAHs (d) in different fish tissues.

Fig. 1 reveals that the highest average residual level for PAH_{16} was found in grass carp; and the lowest PAH_{16} level was in snakehead fish; while the very similar PAH_{16} residual levels were found in crucian carp and silver carp. The average residual levels for LMW-PAHs in the fish species followed the same trends as those for PAH_{16}. The highest residual levels for MMW-PAHs and HMW-PAHs were found in crucian carp, followed by grass carp and silver fish; and the lowest MMW-PAHs and HMW-PAHs levels were in snakehead fish. However, the differences in the average residual levels on wet weight base for PAH_{16}, LMW-PAHs, MMW-PAHs and HMW-PAHs within four fish species were not statistically significant ($P > 0.05$) (Table 2).

Fig. 2 illustrates that the highest average residual levels for PAH_{16} and LMW-PAHs on wet weight base were found in the brain tissue; while the similar average residual levels for PAH_{16} and LMW-PAHs levels were found in the muscle, gill and liver tissues. The average HMW-PAHs residual level was highest in the liver tissue; and that was similar among the muscle, brain and gill tissues. The average residual levels for LMW-PAHs and HMW-PAHs showed an opposite trends in the brain and liver tissues, indicating the higher LMW-PAHs level and the lower HMW-PAHs level in the brain, and the lower LMW-PAHs level and the higher lower HMW-PAHs in the liver. The differences in the average residual levels for PAH_{16}, LMW-PAHs and HMW-PAHs within four fish tissues were statistically significant ($P < 0.01$) (Table 2). However, there was no statistic difference in the average MMW-PAHs residual levels within four fish tissues (Table 2 and Fig. 2).

Compared with the similar studies, the PAH_{16} contents in the freshwater fishes with mean level of 39 ng/g ww ranging from 4.764 to 144.254 ng/g ww in the present study are in the same order of magnitude as those found in Bolti fish and mallet fish collected from markets in Ismailia city, Egypt (19.7–154.3 ng/g ww) (Loutfy et al., 2007), and in the freshwater and marine fishes collected from Hong Kong market (15.5–118 ng/g ww) (Cheung et al., 2007). The PAH_{16} residual levels in the present study were lower than that in freshwater fishes from Pearl River delta, China (30.94–410.06 ng/g ww) (Dong et al., 2006). The PAH_{16} residual levels in the liver tissues in the present study (20.1–29.0 ng/g ww) are also in line with those found in the high mountain lakes (2.1–65.4 ng/g ww) (Vives et al., 2004).

From Figs. 1 and 2, and Table 1 we can see that the residual levels in the different tissues in four fish species, grass carp, snakehead fish, crucian carp and silver carp have different features. Highest residual levels were found in the brain tissues of grass carp, snakehead fish and silver carp, while that was found in the muscle tissue of crucian carp. These differences might be caused by the physical–chemical characters of PAHs (e.g. Kow), and by the lipid content, enrichment and/or metabolism capacities of each fish tissues (please see Section 3.3 for details).

3.2. PAHs distribution and composition pattern

The distribution and composition patterns of 16 priority PAH congeners in the different tissues of each fish species are presented in Figs. 3 and 4, respectively. The interrelationships among the log-transformed contents of PAH congeners in the different fish tissues and in the different fish species are shown in Figs. 5 and 6, respectively.

Fig. 3 reveals that there were very similar distribution patterns of PAH congeners in the different tissues of each fish species. LMW-PAHs including Phe, Ant, Nap and Flo were dominant PAHs congeners, and distributed mainly in the brain and muscle tissues. HMW-PAHs compounds including Bap, Icdp, Daha, Bghip were usually undetectable in the muscle and brain tissues, and distributed primarily in the liver tissues. Chr was dominant in MMW-PAHs compounds, and distributed mainly in the liver and brain tissues.

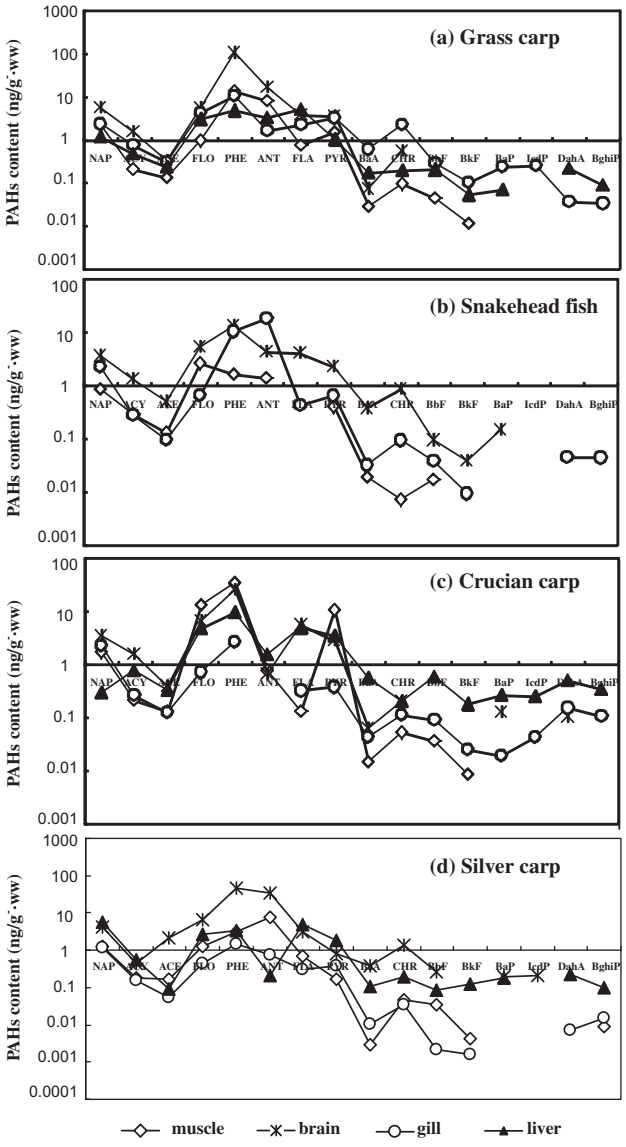

Fig. 3. Distribution pattern of PAH congeners in the grass carp (a), snakehead fish (b), crucian carp (c), and silver carp (d) from Lake Small Bai-Yang-Dian.

Fig. 4 illustrates that, among different PAHs congeners, two- to three-ring LMW-PAHs predominated the distribution in fish tissues with the range of 75.75–98.15%, accounting for 89.97% of total PAHs. Four-ring MMW-PAHs with the range of 1.79–22.33%, and five- to six-ring HMW-PAHs with the range of 0–4.78% only accounted for 8.85% and 1.18% of total PAHs, respectively. On average, the highest percentage of LMW-PAHs was found in the brain tissue (94.08%), followed by the muscle (92.22%), gill (87.59%) and liver (84.65%); the highest percentage of MMW-PAHs was found in the liver tissue (12.29%), followed by the gill (10.63%), muscle (7.76%), and brain (5.59%); the highest percentage of HMW-PAHs was found in the liver tissue (3.06%), followed by the gill (1.78%), brain (0.33%), and muscle (0.02%). Phe with the range of 16.17–73.41% was the most dominant component, according for 37.79% of total PAHs, followed by Ant (18.59%) with the range of 1.04–54.47%, Flo (12.59%) with the range of 1.99–35.27%, Nap (10.79%) with the range of 1.04–30.92%, Fla (9.82%) with the range of 0.22–25.47%, and Pyr (6.43%) with the range of 0.8–16.95%.

Figs. 5 and 6 demonstrate that there were statistically significant positive interrelationships among the log-transformed PAHs contents in the different tissues of each fish species and in the

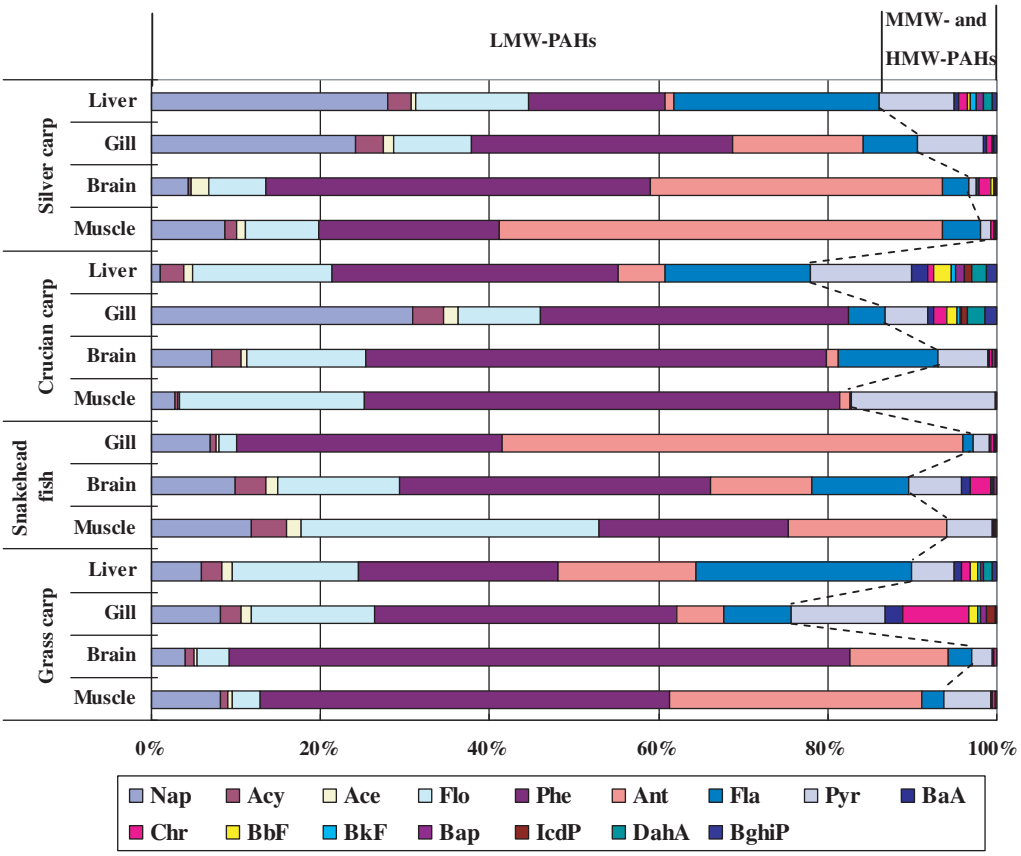

Fig. 4. Percentage composition of 16 priority PAHs congeners in the different tissues of four fish species from Lake Small Bai-Yang-Dian.

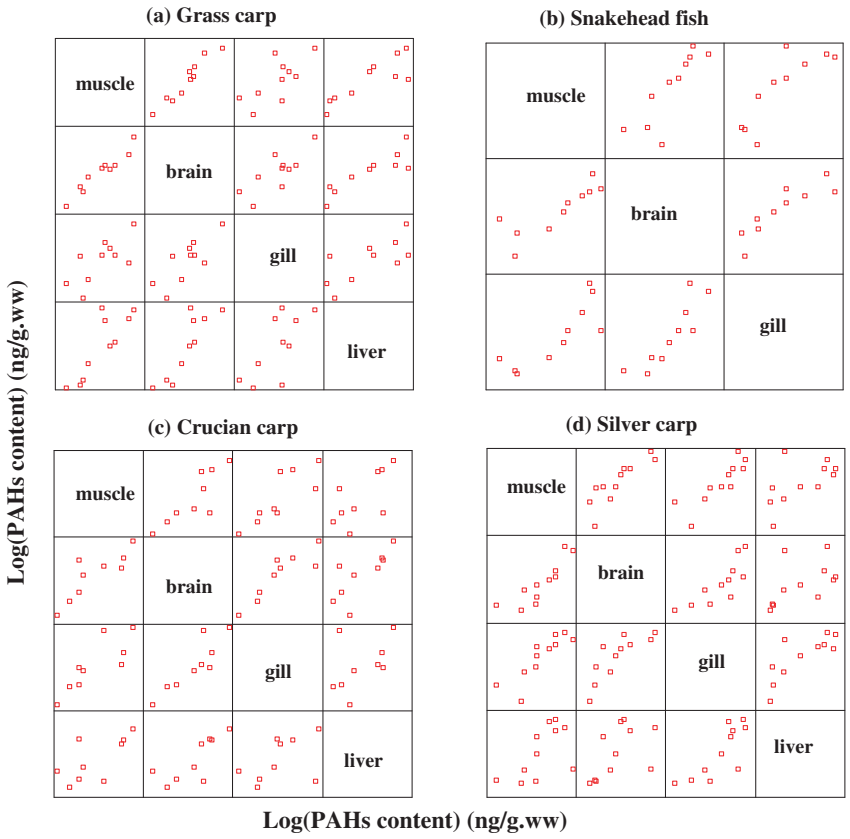

Fig. 5. Matrix relation diagram for the relationships among log-transformed PAHs contents in the different fish tissues.

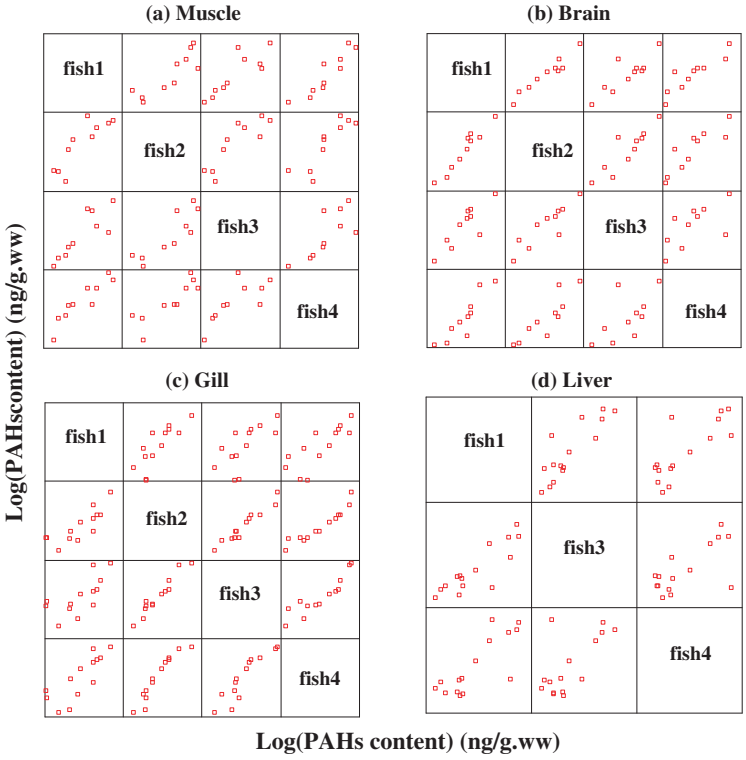

Fig. 6. Matrix relation diagram for the relationships among the log-transformed PAHs contents in the different fish species, fish 1: grass carp; fish 2: snakehead fish; fish 3: crucian carp; fish 4: silver carp.

different fish species of each tissue ($P < 0.01$ or $P < 0.05$) with the Pearson correlation coefficients of 0.58–0.97, respectively. The similar portions of one to one in the log-transformed PAHs contents were found among the different fish tissues and among the different fish species. These results express that there were very similar distribution patterns of PAHs among different fish tissues.

In our previous study in Lake Small Bai-Yang-Dian (Zhu et al., 2009), LMW-PAHs was also found to be predominant in various environmental medium (water, suspended solids and sediment), with the percentage of more then 80% of total PAHs; Phe was also the most prevalent parent compound in suspended solids and sediment. The predominance of Phe in the present study is consistent with other freshwater (Pointet and Milliet, 2000; Vives et al., 2004) and marine systems (Baumard et al., 1998). Such PAHs distribution pattern with the LMW-PAHs predominance of total PAHs would indicate that the major sources of PAHs were the low temperature combustions of coal and biomass fuels (straw, firewood) (Schneider et al., 2001; Mai et al., 2002).

3.3. *Effects of lipid and Kow on PAHs residues and distribution*

The lipid contents in the different tissues of each fish species and in the four tissues are showed in Fig. 7. The lipid-normalized contents of total PAHs (PAH_{16}), LMW-PAHs, MMW-PAHs and HMW-PAHs in four fish tissues and their ANOVA results are presented in Fig. 8 and Table 3, respectively. The relationship between lipid contents and PAH_{16} in the fish tissues is showed in Fig. 9. The relationships between LogKow and log-transformed PAHs contents on wet weight base in the different tissues of each fish species and Log(liver/muscle) ratios as well as Log(liver/brain) ratios are illustrated in Figs. 10 and 11, and Table 4, respectively.

Fig. 7 shows that the highest lipid contents were found in the brain tissues with the average percentage of 24.46% and ranging from 19.50% in crucian carp to 28.00% in silver carp, followed by the liver tissues with the average percentage of 10.17% and ranging

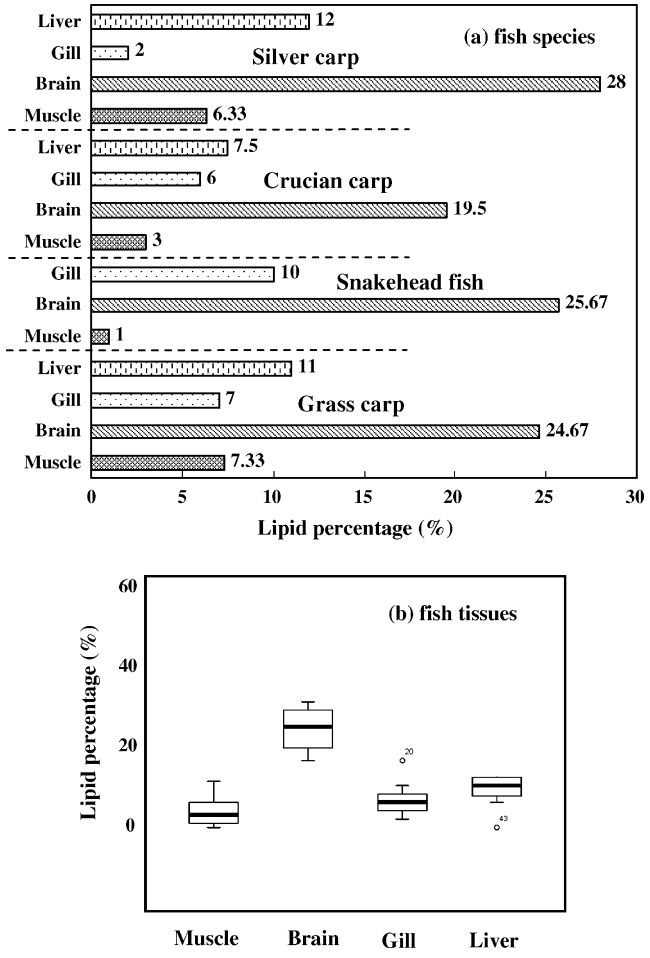

Fig. 7. Lipid contents in the fish species (a) and in the fish tissues (b).

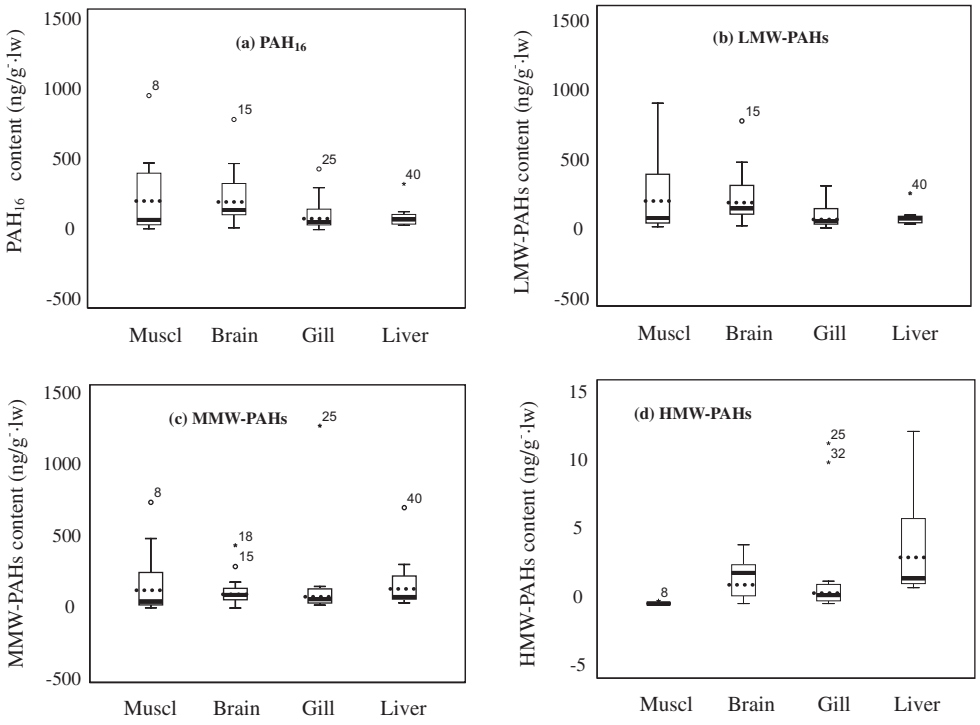

Fig. 8. Lipid-normalized contents of total PAHs (PAH16) (a), LMW-PAHs (b), MMW-PAHs (c) and HMW-PAHs (d) in four fish tissues from Lake Small Bai-Yang-Dian.

Table 3
ANOVA results for the lipid-normalized PAHs contents in fish species and tissues.

PAHs	Source of variation	Mean square	*F* value	*P* value
PAH_{16}	Fish species	7286816.532	0.580	0.632**
	Fish tissues	15548303.441	1.238	0.310**
LMW-PAHs	Fish species	4047170.430	0.485	0.695**
	Fish tissues	12298810.953	1.473	0.238**
MMW-PAHs	Fish species	478386.151	0.876	0.463**
	Fish tissues	388316.261	0.711	0.552**
HMW-PAHs	Fish species	914.034	1.294	0.291**
	Fish tissues	2610.988	3.696	0.020*

The meanings for LMW-PAHs, MMW-PAHs and HMW-PAHs refer to Table 1.
* Significant difference at the significance level of 0.01 ($P < 0.05$).
** No significant difference ($P > 0.05$).

from 7.5% in crucian carp to 12.00% in silver carp, and by the gill tissues with the average percentage of 6.25% and ranging from 2% in silver carp to 12.00% in snakehead fish. The lowest lipid contents were found in the muscle tissues with the average percentage of 4.42% and ranging from 1.0% in snakehead fish to 7.33% in grass carp. Compared Fig. 7(b) with Fig. 2(a), it could be found that the fish tissues with higher percent lipid contented the higher levels of PAH_{16}. When PAHs concentrations were normalized by the lipid contents, the difference in the tissue contents disappeared for PAH_{16} and LMW-PAHs, as indicated by significance values (*P*) decreasing from

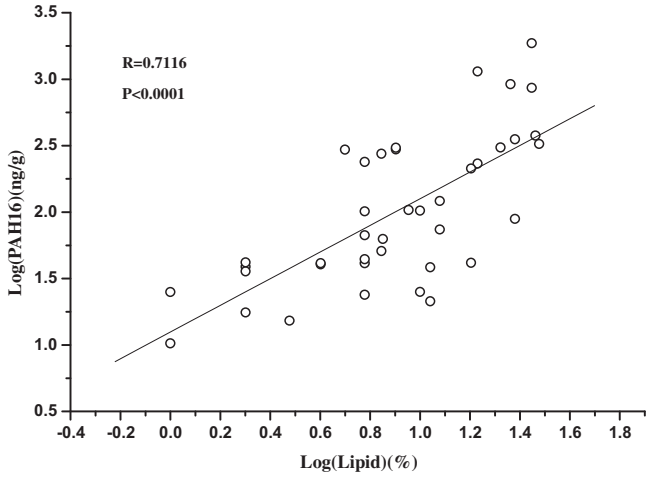

Fig. 9. Relationship between lipid contents and total PAHs (PAH16) in fish tissues.

less than 0.01 to more than 0.3 (Fig. 8 and Table 3). There was a significant positive relationship ($R = 0.7116$, $P < 0.0001$) between lipid contents and PAH_{16} (Fig. 9). These results imply that the lipid content of tissues could be an important factor in the accumulation of lipophilic PAHs by fishes.

Table 4
Relationships and significant levels between LogKow and $LogPAH_{16}$ contents in different tissues of each fish species.

		Muscle	Brain	Gill	Liver	Liver/muscle	Liver/brain
Grass carp	*R*	−0.633	−0.685	−0.752	−0.618	0.548	0.668
	P	0.027	0.029	<0.001	0.014	0.066	0.035
Snakehead fish	*R*	−0.563	−0.748	−0.683	–	–	–
	P	0.090	0.003	0.005	–	–	–
Crucian carp	*R*	−0.625	−0.500	−0.654	−0.298	0.679	0.397
	P	0.022	0.117	0.008	0.262	0.038	0.227
Silver carp	*R*	−0.733	−0.653	−0.806	−0.546	0.492	0.095
	P	0.004	0.021	<0.001	0.035	0.087	0.768

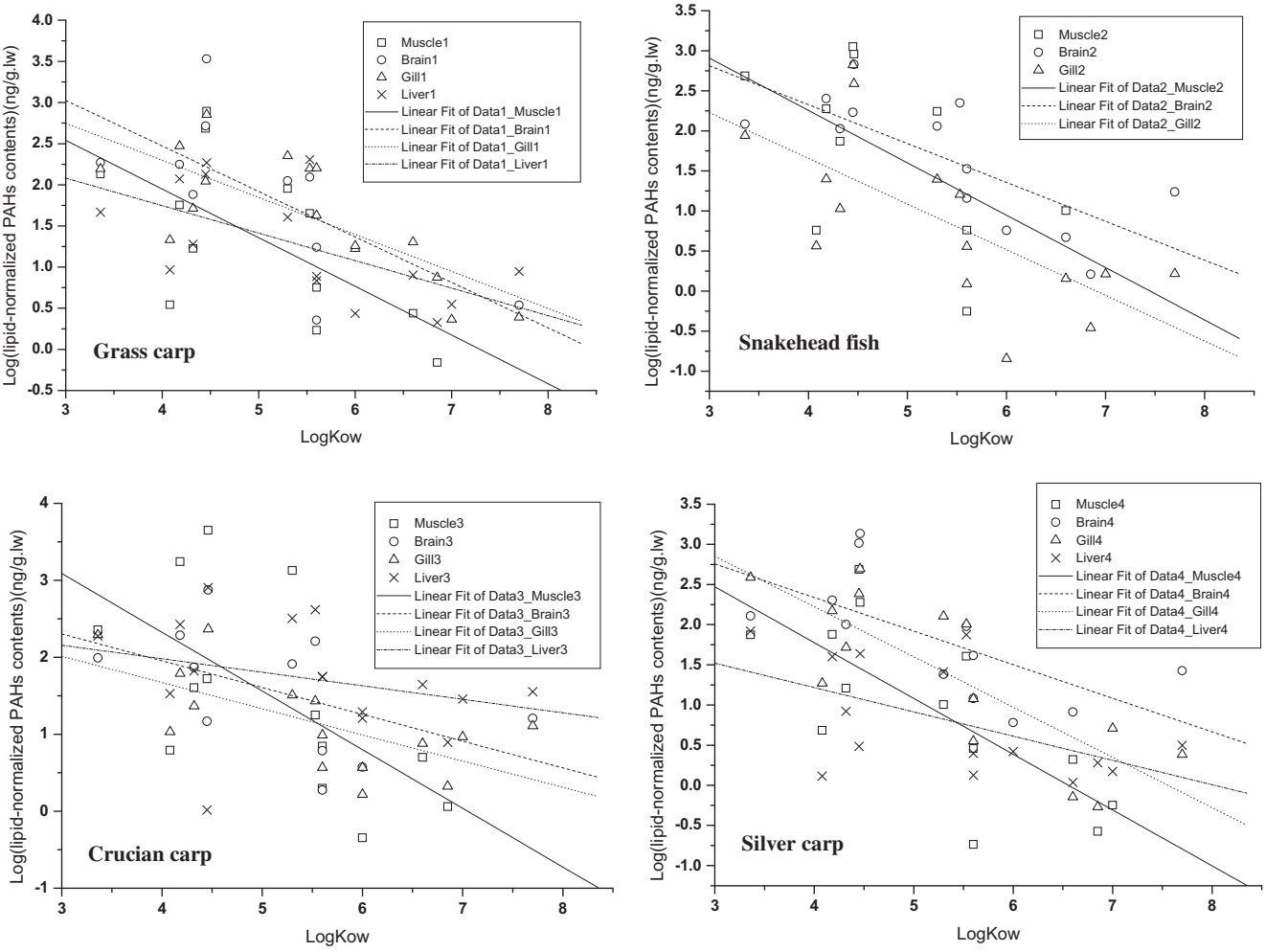

Fig. 10. Relationships between Kow and lipid-normalized PAHs contents in the different tissues of each fish species from Lake Small Bai-Yang-Dian.

It can be seen from Fig. 10 and Table 4 that, negative relationships were found between LogKow and log-transformed PAHs contents on wet weight base in the different tissues of each fish species, with Pearson correlation coefficients varying from −0.298 to −0.8.6. The relationships were statistically significant ($P < 0.05$) for all fish tissues except for the muscle tissue of snakehead fish, and for the brain and liver tissues of crucian carp. The slopes for the muscle tissues of each fish species were largest than the other tissues, indicating Kow affected the PAHs contents in the muscle tissues most (Fig. 10). There were positive relationships between LogKow and Log(liver/muscle) ratios for each fish species with Pearson correlation coefficients varying from 0.492 to 0.0.679. However, the

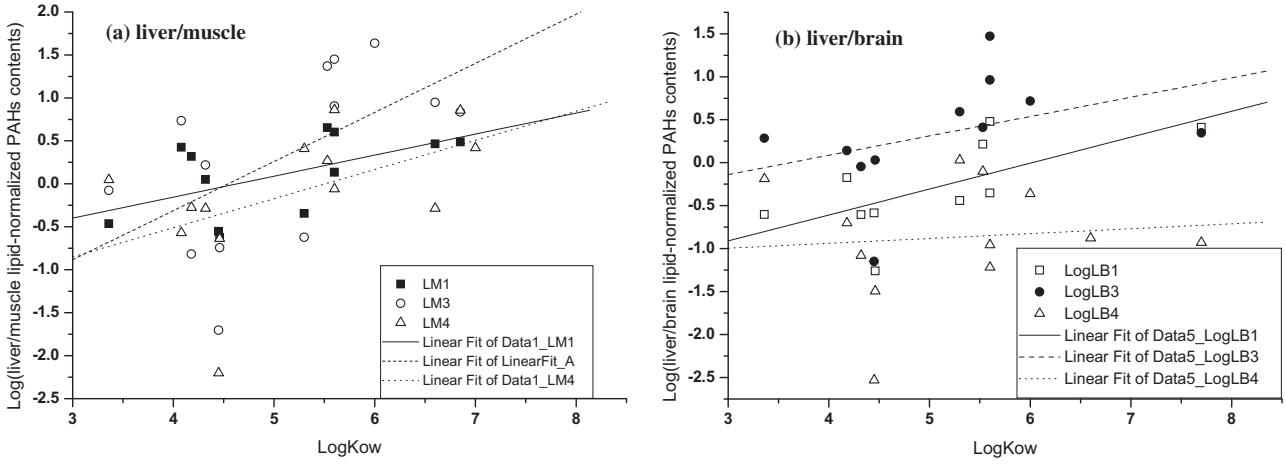

Fig. 11. Relationships between LogKow and Log(liver/muscle) (a) as well as Log(liver/brain) (b) PAHs contents on lipid weight base in different fish species. LM1, LM3 and LM4 represent the liver/muscle for grass carp, crucian carp and silver carp, respectively. LB1, LB3 and LB4 represent the liver/brain for grass carp, crucian carp and silver carp, respectively.

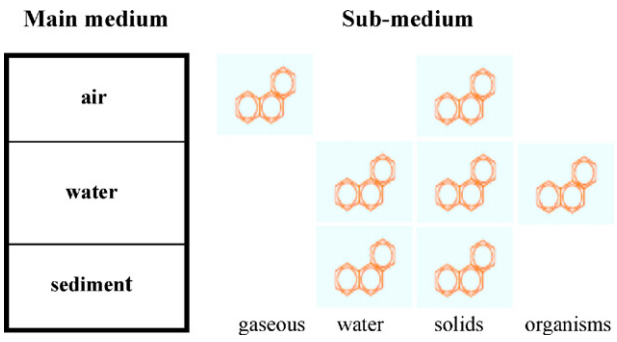

Fig. 12. The Level III fugacity model framework for describing the distribution and fats of PAHs in Lake Small-Bai-Yang-Dian.

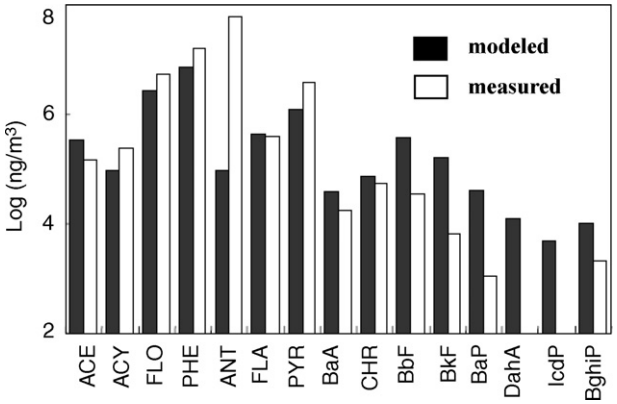

Fig. 13. The comparisons of measured and modeled contents of PAH congeners in fish from Lake Small-Bai-Yang-Dian.

relationships were statistically significant ($P < 0.05$) only for crucian fish (Fig. 11, Table 4). There was significant positive relationship ($R = 0.668$, $P = 0.035$) between LogKow and Log(liver/brain) ratio for grass carp, implying more PAHs accumulation in the liver tissue with the Kow increase. No statistically significant differences were found between LogKow and Log(liver/brain) ratios for crucian carp and silver carp (Fig. 11, Table 4).

The above results indicate that the PAHs residues and distribution in fish tissues are mainly dependent on both the physical–chemical characters of PAHs (e.g. Kow) and tissue lipid content. However, the enrichment and/or metabolism capacities of different fish tissues would also have important effects, especially for curcian carp with highest lipid content in the muscle tissue and but highest total PAHs residual level in the brain tissue.

3.4. Modeling the distributions of PAH congeners in fish

A level III fugacity model was applied to describe the distribution and fats of PAHs in multi media including fish in Lake Small Bai-Yang-Dian. Based on an approach of Mackay and Paterson (1991), three bulk compartments including air (air, particulates), water (water, suspended solids, macrophytes and fishes), and sediment (water and solids) were included. The model framework was presented in Fig. 12. The following main processes were taken into consideration: the advective air flows in/out the air cell from/to outside of Lake Small Bai-Yang-Dian area, the advective water flows in and out of Lake Small Bai-Yang-Dian, the diffusion, dry deposition, and wet precipitation from air to water, the diffusion from water to air, the diffusion between water column and bottom sediment, the sedimentation of suspended solids from water column to sediment, the resuspension of solids from sediment to water column, and the degradation in sediment. The concentration of PAHs in the compartments and the transfer flues between adjacent components were modeled. Monte Carlo simulation was used for uncertainty analysis. The details on modeling the distribution and transfer flues in multimedia in Lake Small Bai-Yang-Dian will be presented in a separate paper.

The comparisons of measured and modeled contents of PAH congeners in fish and the uncertainty analysis of the modeled contents were presented in Figs. 13 and 14, respectively. Fig. 13 shows that there were very similar distribution pattern between measured and modeled contents of PAH congeners in fish. For the most PAH congeners with low molecular weight, the modeled contents were lower than the measured values; however for the most PAH congeners with medium and large molecular weight, the modeled contents were higher. The modeled contents for ACE, FLA, BaA and CHR were slight higher than the measured values; while those for BbF, BkF and BaP were higher by 1–2 log-units than the measured values. It can be seen from Fig. 14 that the variance coefficients of modeled contents for PAH congeners with low molecular weight were much lower than those for PAH congeners with medium and large molecular weight. This implies that the uncertainty of modeled contents for PAH congeners with medium and large molecular weight were much higher.

3.5. Human heath risk of PAHs though fish consumptions

According to the guideline of USEPA (1993, 2000), the following two steps were followed in the present study to assess the human health risk of PAHs though fish consumptions. Firstly, the screening values (SVs) for BaP (BaP) were calculated to measure the risk of human consumption of fishes. Secondly, the potency equivalent concentration (PEC) of total PAHs was calculated for each sample for comparison with the screening value for BaP (BaP SVs).

SV is defined as the concentration of chemical in edible tissue that is of potential public health concern (USEPA, 2000). The SVs for PAHs were calculated as follow (Cheung et al., 2007):

$$\mathrm{SV} = \frac{(\mathrm{RL}/\mathrm{SF}) \times \mathrm{BW}}{\mathrm{CR}} \quad (1)$$

where SV is screening value ($\mu g\, g^{-1}$) that it is used as threshold value against tissue residue level of contamination in similar tissue collected from the environment (USEPA, 2000); SF is oral slope factor $(\mu g\, g^{-1}\, day^{-1})^{-1}$, which is used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime (70 years) exposure to a particular level of a potential carcinogen (USEPA, 1989); RL is maximum acceptable risk level (dimensionless); BW and CR are body weight (kg) and consumption rate (g/day), respectively

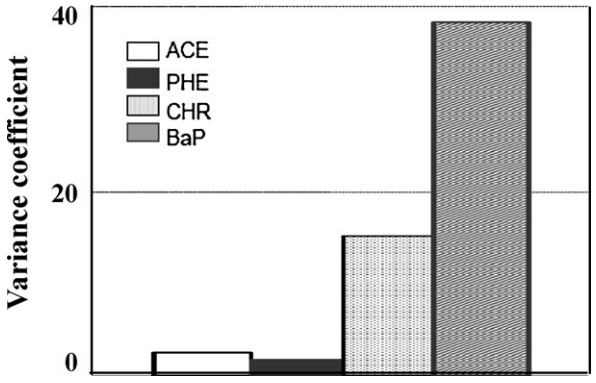

Fig. 14. The variance coefficient of modeled contents of PAH congeners in fish from Lake Small-Bai-Yang-Dian.

According USEPA (1989, 1993, 2000), body weight (BW) was chosen at 70 kg which is the average body weight for adult population; consumption rate (CR) for fishes and oral slope factors (SF) of PAHs were chosen as 142.2 g/day and 7.30 $(\mu g\, g^{-1}\, day^{-1})^{-1}$, respectively; maximum acceptable risk level (RL) was chosen at 10^{-5}, which means that the increased risk would be at most one additional cancer death per 100,000 persons if a person weighing 70 kg consumed 142.2 g of fish per day with the same concentration of contaminant for 70 years (USEPA, 1989).

Based on the above data for RL, SF, BW and CR set by ESEPA, it was recommended that the guideline concentration (SV) is 0.67 ng BaP/g or PEC of total PAHs/g wet wt for human fish consumption (USEPA, 2000). The health risk level of total PAHs though fish consumptions would be estimated through the comparison of the potency equivalent concentration (PEC) of total PAHs with the screening value for BaP (BaP SVs). If the PEC of total PAHs in fish samples exceeds the screening value (0.67 ng/g wet wt), the health risk of total PAHs through fish consumptions would be higher then the maximum acceptable risk level (RL) (10^{-5}); otherwise, it would be lower then 10^{-5}. Also, the actual risk level (ARL) of total PAHs could be calculated accurately by the following expression deduced from Eq. (1).

$$\mathrm{ARL} = \frac{\mathrm{PEC} \times \mathrm{SF} \times \mathrm{CR}}{\mathrm{BW}} \quad (2)$$

were ARL is the actual risk level of total PAHs through fish consumptions (dimensionless); the meanings for the SF, BW and CR are same as the Eq. (1); PEC is the potency equivalent concentration of total PAHs for comparison with the screening value for BaP (USEPA, 1993), and it can be calculated using the following equation (Nisbet and Rasmussen, 1992):

$$\mathrm{PEC} = \sum(\mathrm{RP} \times C) \quad (3)$$

where RP is equal to relative potency for each PAHs and C is equal to concentration of each PAH. According to Nisbet and Rasmussen (1992), the relative potency (RP) is 0.001 for Nap, Acy, Ace, Flo, Phe, Fla and Pyr, 0.01 for Ant, Chr and BghiP, 0.1 for BaA, BbF, BkF and IcdP, 1 for BaP, and 5 for DahA.

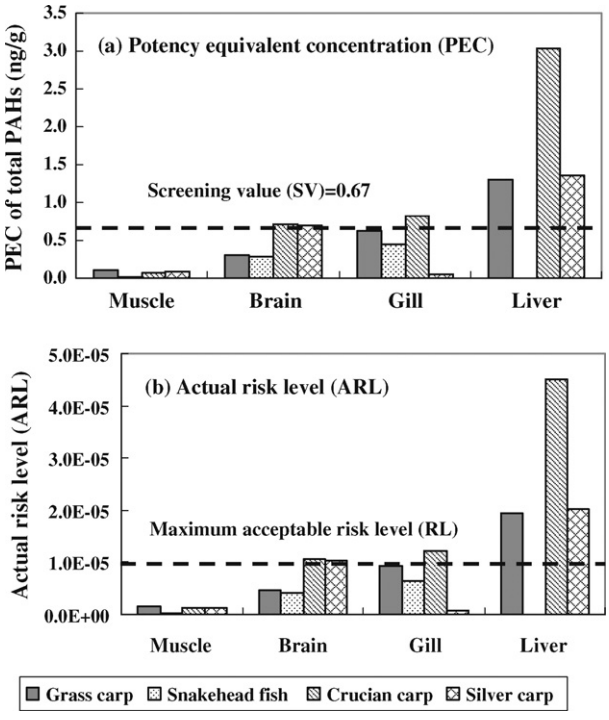

Fig. 15. Potency equivalent concentration (PEC) (a) and actual risk level (ARL) (b) of total PAHs for the tissues of each fish species from Lake Small Bai-Yang-Dian.

The PEC and actual risk level of total PAHs in the different tissues of each fish species are calculated by Eqs. (3) and (2), and are presented in Fig. 15. It can be seen from Fig. 15(a) that the PEC values of total PAHs for all studied fish muscle tissues and for the brain tissues of grass carp and snakehead fish were all below the screening value of 0.67 ng/g wet wt; while these for the brains of crucian carp and silver carp exceeded this screening value. The results imply that the risk levels of total PAHs are lower than 10^{-5} for the human consumption of all fish muscles and the brains of grass carp and snakehead fish. However, the risk levels of total PAHs were higher than 10^{-5} for the human consumption of the brains of crucian carp and silver carp (Fig. 15(b)). The PEC values of total PAHs in the liver tissues of all studied fishes except for snakehead fish exceeded the USEPA screening value (0.67 ng/g wet wt) for 2–4.5 times (Fig. 15(a)), indicating the risk levels of total PAHs being much higher than 10^{-5} for the human consumption of these fish liver tissues (Fig. 15(b)). Fortunately, it is infrequent for human to eat fish livers. However, the PEC levels of total PAHs in all studied fish tissues of the present study were still lower than the maximum permissible BaP limit for crops and baked meat (5 ng/g) and for plants (10 ng/g)) in the national criterions (Wu et al., 2005).

4. Conclusions

The residual levels, distribution and composition of PAHs in the liver, brain, gill and muscle tissues of four freshwater fish species, and their effect factors were analyzed. The human health risk of PAHs though fish consumptions was estimated. It could be concluded that the residual levels of PAHs on wet weight base varied among both the fish species and the fish tissues, which were dependent on both the Kow of PAH congeners and the lipid contents in fish tissues. The differences in the residual levels within four studied fish species were not statistically significant ($P > 0.05$); however, these within four fish tissues were statistically significant ($P < 0.01$). There were very similar distribution patterns of PAH congeners among both the fish tissues and the fish species, with the predomination of LMW-PAHs. There was a significant positive relationship between lipid contents and PAHs residual levels in the fish tissues. The risk levels of total PAHs exceeded 10^{-5} for some tissues, such as the liver tissues and the brains tissues of crucian carp and silver carp. The distributions of PAH congeners in fish could be simulated by a level III fugacity model, especially for low molecule weight PAHs.

Acknowledgments

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