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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.