Concentration Levels and Potential Ecological Risks of Polycyclic Aromatic Hydrocarbons in Chinese Rivers

Chenglian Feng · Qian Luo · Zijian Wang

Received: 8 December 2008 / Revised: 3 February 2009 / Accepted: 10 February 2009 / Published online: 4 March 2009
© Springer Science+Business Media B.V. 2009

Abstract Polycyclic aromatic hydrocarbons (PAHs) are one of the most important persistent organic pollutants (POPs) and are widespread in surface waters in China. Based on the literature surveyed, concentration levels and geographic distribution of 16 PAHs in major Chinese rivers were summarized. The results showed that 2-3-ring PAHs were predominated in water, 4-ring PAHs were abundant in suspended particular matter (SPM), and 3-6 ring PAHs were the main chemical forms in sediment. In general, concentration levels of PAHs in rivers from northern China were higher than those from southern China. There existed a significant difference between concentration level of PAHs from the north and from the south. In comparison with concentration levels of PAHs in the world rivers, level of PAHs in dissolved phase in Chinese rivers was higher than those from other countries, while PAHs concentration in SPM and sediment of Chinese rivers was in the middle range. The quotient method was used to screen the potential risk of PAHs to aquatic organisms. It appeared that 7 among 16 PAHs, i.e., phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene and benzo[a]pyrene, might have potential adverse effects to aquatic system, which should be particularly concerned.

Keywords Polycyclic aromatic hydrocarbons (PAHs) · Chinese rivers · Concentration level · Geographic distribution · Ecological risk

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds which mainly contain two or more fused aromatic rings of carbon and hydrogen atoms. As one of the typical persistent organic pollutants (POPs), PAHs are widely distributed in various environmental media which occur in atmosphere, water, soil, sediment and organism (Tao et al. 2004; Nizzetto et al. 2008). The 16 PAHs have been listed as priority control pollutants by US Environmental Protection Agency (Manoli et al. 2000). Due to their toxic, mutagenic and carcinogenic characteristics, PAHs are considered to be hazardous to the biota and surrounding environment. The primary environmental sources of PAHs include both anthropogenic inputs and biological conversion of biogenic precursors (Means et al. 1980). PAHs can enter into the environment through various routes. Fossil fuel incomplete combustion, oil spills, domestic and industrial wastewater discharges, as well as atmospheric fallout of vehicle exhaust and industrial stack emission, have caused significant accumulation of PAHs in aquatic environment (Broman et al. 1991; Na'f et al. 1992; Countway et al. 2003; Gu et al. 2003; Fang et al. 2007). For environmental management, understanding the behavior of PAHs and their environmental risk to ecological systems, especially for aquatic environment, is necessary.

Organic contaminants in aquatic system may exist in several forms, including free dissolved phase, the phase bounded to dissolved organic matter (DOM), adsorbed to suspended particulate matter (SPM), and associated with sediments (Zhou and Maskaoui 2003). The distribution of PAHs in aquatic multimedia is mainly controlled by their intrinsic physical-chemical properties, such as solubility, vapor pressure and adsorption coefficient. The environmental fate and behavior of PAHs are ultimately determined

C. Feng · Q. Luo · Z. Wang (✉)
State Key Laboratory of Environmental Aquatic Chemistry,
Research Center for Eco-Environmental Sciences, Chinese
Academy of Sciences, P.O. Box 2871, Beijing 100085, China
e-mail: wangzj@rcees.ac.cn

Fig. 1 The map of the seven major river basins in China

by their physical-chemical properties and sediment characteristics (Readman et al. 1984; Mitra and Dickhut 1999; Mackay 2001). Owing to their low aqueous solubility and hydrophobic nature, these compounds are strongly adsorbed to the particles associated with the organic compounds of solid phase matrix, which will finally be deposited to the underlying sediments of estuary, lake and marine (Tolosa et al. 2004).

There are seven major river basins in China, which are: the Yangtze River basin, the Yellow River basin, the Pearl River basin, the Liaohe River basin, the Haihe River basin, the Huaihe River basin and the Songhuajiang River basin (Fig. 1). The rapidly developing industrial and agricultural activities, municipal development and the use of chemicals have caused heavy loads of POPs to aquatic system, which have adversely affected the biological organism (Liu et al. 2000; Manz et al. 2001; Fu et al. 2003; Tao et al. 2003; Zhang et al. 2003). As for PAHs, many studies determined concentrations and sources of PAHs in natural waters all over the world (Fernandes et al. 1997; Kim et al. 1999; Manoli and Samara 1999; Soclo et al. 2000; Notar et al. 2001; Maskaoui et al. 2002; Doong and Lin 2004; Luo et al. 2006; Qiao et al. 2006; Guo et al. 2007; Liu et al. 2008). In China, intense industrial and commercial

activities in the coastal area caused adverse effects on the aquatic system (Zhang et al. 2007). In the past few decades, numerous studies have been conducted in order to determine the contamination status and the spatial distribution of PAHs in surface waters (Cao et al. 2005; Li et al. 2006; Feng et al. 2007). The major investigations focused on PAHs concentrations of coastal water and sediments (Mai et al. 2001; Zhou and Maskaoui 2003). In addition, PAHs concentration levels of inland rivers in some big cities, such as Tianjin city in northern China and Hangzhou city in southern China, were also investigated (Shi et al. 2005; Zhu et al. 2004).

In this paper, we reviewed the published literature about PAHs concentration levels of main rivers in China and analyzed the distribution characteristics of PAHs in water, sediment and SPM, respectively. Meanwhile, the concentration levels of PAHs in Chinese rivers and some rivers in other countries were compared. The results could give an overview of PAHs in Chinese fresh water system. Furthermore, it could provide strong scientific data support to the technologies and measures on PAHs pollution prevention and treatment for rivers and lakes in China.

Method Used to Derive PAHs Concentration

Sources of Data

The concentration levels of PAHs in different rivers of China were compiled and summarized from the peer-reviewed literature. All available papers investigating PAHs and published from 2000 to 2008 were screened; and relevant papers containing PAHs concentration were reviewed in detail for valid data.

Data Selection Criteria

For the purpose of ranking data, the regulations are as follows: First, studies described in the literature are conducted according to or on the basis of valid or international accepted, standardized methodology, including US EPA method or modified US EPA methods. Approaches for the determination of PAHs include those using both high performance liquid chromatographic (HPLC) with fluorescence detector or ultraviolet detector, and gas chromatographic-mass spectrometry (GC/MS) (US EPA Method 610 2008; Wang et al. 2007). Second, the literature should have a clear description about quality assurance (QA) and quality control (QC). All data are subjected to strict regime of quality control procedures. Replicate samples are examined in PAHs analysis to further monitor the precision of analytical results (Luo et al. 2004). And then, the recovery value should be in agreement with US EPA methodology protocol. Third, the data described in the papers should be representative. The samples should be collected from the typical river cross sections which could represent PAHs concentrations in the overall or part of the rivers. In the literature surveyed, abnormal data concerning sewage channel, drainage area, seriously polluted sites and harbors are ignored, so as to exactly explain the whole PAHs concentration level in the river watershed.

Results and Discussion

PAHs Concentrations in Water (Dissolved Phase)

A wide range of research about PAHs distribution in rivers and other surface waters in China have been published in the last decade. The concentrations of PAHs in water from the main rivers at different sampling sites were listed in Table 1. Previous studies indicated that 16 PAHs were detectable in many water samples. It could be seen from those studies that the detection rates of low-ring PAHs compounds were usually greater than the high-ring PAHs, with naphthalene being the highest. It could also be found that 3-ring and 4-ring PAHs, including fluorene, phenanthrene, anthracene, fluoranthene and pyrene, were the most abundant compounds in all water samples. The detection rates of 5-ring and 6-ring PAHs, including benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, were much lower. Among the individual PAHs, the dissolved concentration of 2-ring naphthalene in the rivers of Tianjin city was the highest, reaching up to 32.432 µg/L (Cao et al. 2005). For individual 3-ring to 6-ring PAHs, the highest concentration occurred in Liaohe River (Guo et al. 2007), of which pyrene was the highest (2.463 µg/L). Of all the surface water samples, the PAHs concentration in the Pearl River was relatively lower, except for naphthalene, with its mean value of 2.552 µg/L (Luo et al. 2004). As to the other 15 PAHs in the Pearl River, the concentrations were relatively lower than those in other rivers, except for the concentration of phenanthrene (0.0107 µg/L). As for the northern rivers in China, such as the Liaohe River basin and Haihe River basin, concentration of individual PAHs was much higher than that in the southern Chinese rivers, such as the Yangtze River (Feng et al. 2007), the Pearl River (Luo et

Table 1 The statistical summary of ΣPAHs concentration in surface water of Chinese rivers (µg/L)

Sampling sites	Sample number	Minimum concentration	Maximum concentration	Mean concentration	90th percentile	References
Jiulong River, Estuary	17	6.96	26.9	17.062	24.820	Maskaoui et al. (2002)
Surface water, Hangzhou	17	0.989	9.663	3.717	7.123	Chen et al. (2004)
Gaoping River, Taiwan	48	0.01	9.4	0.43		Doong and Lin (2004)
The Pearl River, Delta	12	0.691	6.458	2.715	6.335	Luo et al. (2004)
Macao harbor	6	0.691	6.458	3.941	6.458	Luo et al. (2004)
Tonghui River, Beijing	16	0.193	2.651	0.762		Zhang et al. (2004)
The Rivers, Tianjin	10	0.058	1.060	0.259	1.0123	Shi et al. (2005)
The Qiantangjiang River	180	0.070	1.844	0.283		Chen et al. (2007)
The Yangtze River	11	0.242	6.235	1.452	5.605	Feng et al. (2007)
The Liaohe River	16	0.946	13.449	6.445	13.060	Guo et al. (2007)
The Yellow River	26	0.144	2.361	0.662	1.664	Sun et al. (2008)

Table 2 The statistical summary of Σ PAHs concentration in SPM and sediment of Chinese rivers ($\mu\text{g/g}$)

Medium	Sampling sites	Sample number	Minimum concentration	Maximum concentration	Mean concentration	90th percentile	References
SPM	Macao harbor	6	0.093	0.256	0.183	0.256	Luo et al. (2004)
	The Rivers, Tianjin city	10	0.938	46.3	12.846	43.02	Shi et al. (2005)
	The Pearl River Delta	21	0.442	16.489	1.659	1.797	Luo et al. (2006)
	Surface waters, Hebei Province	37	0.60	171.9	17.3		Bai et al. (2007)
	The Yangtze River	9	0.095	8.798	3.556	8.798	Feng et al. (2007)
	The Liaohe River watershed	16	0.318	238.52	21.725	100.895	Guo et al. (2007)
	The Yellow River	26	0.507	10.51	4.101	8.860	Sun et al. (2008)
sediment	Jiulong River Estuary	9	0.059	1.177	0.334	1.177	Maskaoui et al. (2002)
	Surface water, Hangzhou	11	0.133	7.343	1.557	6.471	Chen et al. (2004)
	Gaoping River, Taiwan	48	0.001	0.356	0.081		Doong and Lin (2004)
	Tonghui River, Beijing	16	0.127	0.928	0.540		Zhang et al. (2004)
	The Rivers, Tianjin	9	3.41	346	59.967	346	Shi et al. (2005)
	The Huaihe River	18	0.031	1.008	0.294	0.852	He and Yan (2006)
	The Pearl River Delta	9	0.189	0.637	0.368	0.627	Luo et al. (2006)
	The Qiantangjiang River	38	0.091	0.614	0.313		Chen et al. (2007)
	The Yangtze River	30	0.072	3.995	1.335		Feng et al. (2007)
	The Liaohe River watershed	12	0.062	0.841	0.287	0.746	Guo et al. (2007)
	The Haihe River	13	0.775	255.372	27.074	163.168	Jiang et al. (2007)
	The Songhuajiang River	9	0.107	20.331	3.789	20.331	Lu et al. (2007)
	The Yellow River	26	0.016	1.358	0.182	0.735	Sun et al. (2008)

al. 2004) and the Gaoping River in Taiwan (Doong and Lin 2004).

Geographical distribution of dissolved Σ PAHs from the major rivers was shown in Table 1. The concentration of Σ PAHs in Jiulong River was the highest, ranging from 6.96 to 26.9 $\mu\text{g/L}$, with a mean value of 17.062 $\mu\text{g/L}$ (Maskaoui et al. 2002). The Σ PAHs concentration in Liaohe River (Guo et al. 2007), Macao Harbor (Luo et al. 2004) and surface waters in Hangzhou city (Chen et al. 2004) were also higher than those in other rivers, with a mean value of 6.445 $\mu\text{g/L}$, 3.941 $\mu\text{g/L}$ and 3.717 $\mu\text{g/L}$, respectively. It might be probably caused by the well-developed economy and large sewage discharge around these areas.

PAHs Concentrations in SPM

Suspended particulate matter (SPM) is the most active absorbent of PAHs in water bodies. Because of its complicated composition, it can adsorb the organic pollutants in water, moreover, the adsorbed PAHs can also be transferred to the sediments through settlement process. At the same time, SPM may be generated from the sediment's re-suspension. As a result, SPM in the water body plays an important role in PAHs transportation in aquatic multimedia and reflects the PAHs contamination status. However, data on the PAHs dis-

tribution in SPM are much less than those in sediment and in water dissolved phases.

Based on the available data (Table 2), it could be observed that 2-ring to 6-ring PAHs were all detectable in SPM samples, while 3-ring and 4-ring PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) were more abundant. In general, 6-ring PAHs, such as dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, were detected at higher level and the highest concentrations were in Liaohe River, where they were 3.317 $\mu\text{g/g}$, 3.358 $\mu\text{g/g}$, 2.606 $\mu\text{g/g}$, respectively (Guo et al. 2007). Regarding to individual PAHs in SPM, the concentration level varied in different rivers. The highest concentration of naphthalene (226.586 $\mu\text{g/g}$) occurred in one tributary near a heavy industrial area (Taizihe River) in Liaohe River (Guo et al. 2007), which dramatically exceeded other sampling sites in the main course of the same river. The highest concentration of phenanthrene was 88.085 $\mu\text{g/g}$, which was in a lake section of the studied river, close to Tianjin city (Bai et al. 2007). For these individual PAHs in SPM, concentrations in tributaries, lakes, bays, harbors, outfalls were higher than those in main course of rivers.

Σ PAHs concentration in Macao harbor was the lowest, ranging from 0.0925 to 0.256 $\mu\text{g/g}$, with a mean value of 0.183 $\mu\text{g/g}$ (Luo et al. 2004). The highest Σ PAHs concentra-

tion in SPM occurred also in the Liaohe River, ranging from 0.3175 to 238.519 $\mu\text{g/g}$, with a mean of 21.725 $\mu\text{g/g}$, followed by rivers in Hebei province in northern China (mean of 17.3 $\mu\text{g/g}$) and in Tianjin city (mean of 12.846 $\mu\text{g/g}$), respectively. As a result, ΣPAHs concentrations in northern regions of China were higher than those in the southern regions of China. The difference should be due to more coal combustion and more heavy industries in north area, such as in Liaohe River basin and around Tianjin city.

PAHs Concentrations in Sediments

Sediment, as the main destination of PAHs in aquatic environment, reflects a longer-time-period pollution status. Because of the low solubility, most of PAHs could be found in sediment. Adsorbed PAHs may release to water phase and become the secondary contamination source. Surveys on PAHs concentrations in sediment may provide basic data for further ecological risk assessment to aquatic organisms.

As shown in Table 2, PAHs in sediment were mainly dominated by 4-ring and 5-ring PAHs, while concentrations of 2-ring and 3-ring PAHs were relatively lower. Among different water bodies, PAHs concentration in sediments of port, gulf, river estuary and tributaries were higher than those in the main course of rivers. In comparison, PAHs concentration in SPM at the same sampling site of a river was much larger than that in sediment (Luo et al. 2006; Feng et al. 2007; Sun et al. 2008). For one thing, the total organic carbon (TOC) in SPM is possibly higher than that in sediment (Feng et al. 2007); For another, sediment can re-suspend and become SPM, releasing certain amount of organic pollutants into water phase (Yang et al. 2008).

Of all the surveyed rivers, the highest concentration of ΣPAHs concentration occurred in those around Tianjin city and as high as 346 $\mu\text{g/g}$, with a mean value of 59.967 $\mu\text{g/g}$ (Shi et al. 2005), followed by the Haihe River, whose ΣPAHs concentration ranged from 0.775 $\mu\text{g/g}$ to 255.372 $\mu\text{g/g}$, with a mean value of 27.074 $\mu\text{g/g}$ (Jiang et al. 2007). Some rivers in northern China, such as the Songhua-jiang River in Heilongjiang Province and the Tonghui River in Beijing city, PAHs concentrations in sediments were also at higher level, whose mean ΣPAHs concentrations were 3.789 $\mu\text{g/g}$, 0.54 $\mu\text{g/g}$, respectively. Rivers in southern China, such as the Pearl River, the Qiantangjiang River, the Gaoping River in Taiwan and the Jiulong River, PAHs concentrations in sediments were lower than those in northern rivers, except for a few sampling sites. Distribution pattern of PAHs in sediment was similar to that in surface water and in SPM.

Ranking PAHs Concentration in Rivers of the World

Compared with other contaminated rivers in the world (Table 3), the PAHs concentrations in water dissolved phase

of Chinese rivers were much higher than those in Seine River (Fernandes et al. 1997), Mississippi River (Mitra and Bianchi 2003) and Susquehanna River (Ko et al. 2007), some of which even exceeded 100 folds. The results indicated that level of PAHs in water phase of Chinese rivers was higher. It may possibly because of the intense industrial and commercial activities in the studied area in the past few years, which could result in the high loads of PAHs. However, PAHs concentrations in most of SPM samples from Chinese rivers were close to those in Seine River and Mississippi River, except those from Liaohe River (ranging from 0.318–238.52 $\mu\text{g/g}$; mean = 21.725 $\mu\text{g/g}$) and from the rivers in Tianjin area (ranging from 0.938–46.3 $\mu\text{g/g}$; mean = 128.46 $\mu\text{g/g}$). For those rivers in southern China, such as the Pearl River, PAHs concentration level in SPM was similar to those of Seine River and Mississippi River, only slightly higher than that in York River (Countway et al. 2003).

As for the PAHs level in sediment from Chinese rivers and other rivers in the world, most rivers in China, including the Yellow River, the Pearl River and rivers in Hangzhou city, were in the middle position. The concentration level of PAHs was close to rivers such as the River estuaries in Malaysia (Zakaria et al. 2002), Kyeonggi Bay in Korea (Kim et al. 1999), Santander Bay in Spain and Susquehanna River in USA (Viguri et al. 2002; Ko et al. 2007). The highest ΣPAHs concentration in sediment occurred also in China, i.e., in the rivers around Tianjin city (ranging from 3.41 to 346 $\mu\text{g/g}$, mean = 59.967 $\mu\text{g/g}$) (Shi et al. 2005).

On the whole, ranking concentration levels of PAHs in rivers of the world, PAHs level in water dissolved phase in Chinese rivers was a little higher than those in other countries. While in SPM and sediment, PAHs level in Chinese rivers was similar to those rivers in other countries. On the one hand, Chinese rivers are polluted by PAHs to some extent. On the other hand, from the cumulative effects of PAHs in sediment, there is no significant difference between Chinese rivers and the rest of the world.

Spatial Distribution of PAHs

There were significant differences among ΣPAHs concentration in water, SPM and sediment from seven major river basins in China (Fig. 2). For water, the mean concentration of PAHs in Liaohe River basin was the highest (mean = 6.445 $\mu\text{g/L}$) and that in Haihe River was the lowest (mean = 0.259 $\mu\text{g/L}$). For SPM, the mean concentration of PAHs in Liaohe River basin was the highest (mean = 21.725 $\mu\text{g/g}$), followed by that in Haihe River basin (mean = 12.846 $\mu\text{g/g}$), and Yellow River basin (mean = 4.101 $\mu\text{g/g}$). For sediment, the mean concentration of PAHs in Haihe River basin was the highest (mean = 27.074 $\mu\text{g/g}$), followed by the Songhua-jiang River (mean = 3.789 $\mu\text{g/g}$). Higher PAHs concentra-

Table 3 Concentrations of PAHs in water, SPM and sediment from different rivers in the world

Phases	Sampling sites	Sample number	Σ PAHs ($\mu\text{g/L}$; $\mu\text{g/g}$) ^a		References
			Range	Mean	
Water	Seine River, France	6	0.004–0.036	0.02	Fernandes et al. (1997)
	Mississippi River, USA	4	0.006–0.069	0.041	Mitra and Bianchi (2003)
	Surface waters, Hangzhou China	17	0.989–9.663	3.717	Chen et al. (2004)
	Gaoping River, China	48	0.01–9.4	0.43	Doong and Lin (2004)
	Rivers in Tianjin, China	10	0.058–1.060	0.259	Shi et al. (2005)
	Liaohe River, China	16	0.946–13.449	6.445	Guo et al. (2007)
	Susquehanna River, USA	36	0.017–0.15	0.067	Ko et al. (2007)
	The Yellow River, China	26	0.144–2.361	0.662	Sun et al. (2008)
SPM	Seine River, France	11	1–14	5	Fernandes et al. (1997)
	York River estuary, US	20	0.002–0.123	0.02	Countway et al. (2003)
	Mississippi River, US	18	1.3–7		Mitra and Bianchi (2003)
	The Rivers, Tianjin, China	10	0.938–46.3	12.846	Shi et al. (2005)
	Pearl River Delta, China	21	0.442–16.489	1.659	Luo et al. (2006)
	Liaohe River basin, China	16	0.318–238.52	21.725	Guo et al. (2007)
	The Yellow River, China	26	0.507–10.51	4.101	Sun et al. (2008)
Sediment	Kyeonggi Bay, Korea	24	0.009–1.4	0.12	Kim et al. (1999)
	Santander Bay, Spain	16	0.02–344.6		Viguri et al. (2002)
	Malaysia Rivers	25	0.004–0.924		Zakaria et al. (2002)
	Surface waters, Hangzhou, China	11	0.133–7.343	1.557	Chen et al. (2004)
	Gaoping River, China	48	0.001–0.356	0.081	Doong and Lin (2004)
	The Rivers, Tianjin, China	9	3.41–346	59.967	Shi et al. (2005)
	The Pearl River, China	9	0.189–0.637	0.368	Luo et al. (2006)
	Liaohe River, China	12	0.062–0.841	0.287	Guo et al. (2007)
	Susquehanna River, USA	36		3	Ko et al. (2007)
	The Yellow River, China	26	0.016–1.358	0.182	Sun et al. (2008)

^aConcentration of water: $\mu\text{g/L}$; concentration of sediment and SPM: $\mu\text{g/g}$

Fig. 2 Geographic distribution of Σ PAHs among the seven major river basins in China. (The Σ PAHs concentrations used in the figure were the mean values obtained from statistical analysis. Concentration unit of water was $\mu\text{g/L}$; concentration unit of SPM and sediment was $\mu\text{g/g}$. The symbol “*” implies a non-available value)

tions occurred mostly in north China ($p < 0.05$, significant at the 95% confidence level). The geographic distribution also showed that the more contaminated river sites occurred mainly in Liaohe River, Haihe River, and Songhua-jiang River in northern China. The northern rivers distribute in some big industrial cities such as Tianjin city, Beijing city and Shenyang city. For example, the Liaohe River basin in northern China is the important industrial bases with oil, chemical and steel factories, approximately 2074 million tons of industrial and domestic wastewater are discharged annually into the Liaohe River catchment (SEPA of China 2004). For Tianjin city in northern China, which has a population of 10 million, is highly polluted with the development of industry and rapid urbanization. Industry and automobiles are two major sources of PAHs pollution. The industrial corporation burn 15 million tons of coal per year and discharge 180 million tons of wastewater (Tianjin Environmental Protection Bureau 2001), which lead to the high level of PAHs concentration in the rivers (such as Haihe River basin) of Tianjin area. While in southern China, there are less heavy industrial bases than those in northern China. Besides, due to the climate difference between north and south, the lack of winter-heating system in southern China also result in less coal combustion wastes. Parent PAHs have both natural (plant debris, forest and prairie fires) and anthropogenic sources (fossil fuel combustion, etc.). Incomplete combustion of fossil fuels is always treated as a major production process for PAHs. Therefore, from the sources of these compounds, the PAHs concentration level in southern China is relatively lower than the northern China.

Initial Ecological Risk Assessment

Ecological risk assessment has been developed from single-species toxicity test to multi-species toxicity test, then to ecological risk models. In order to assess the potential ecological risk of PAHs to aquatic organism in major rivers of China, the quotient approach was applied to assess the initial ecological risk of PAHs. Quotient approach has been used to illustrate the risk characterization of target compounds (Solomon et al. 2000; Brain et al. 2006). The aquatic species, which exist widely in the Chinese rivers were selected as the ecological receptors, including phytoplankton, zooplankton, invertebrate, fish, etc. According to the selected ecological receptors and the toxic data from the references, the hazard quotients (hazard quotients, HQ) of some potential chemicals were calculated, followed the formulation as follows:

$$HQ = \frac{C_{\text{exposure}}}{TRV},$$

where C_{exposure} is the environmental concentration (assumed as exposure concentration) of selected PAHs, TRV is the toxicity reference value (toxicity reference value, TRV) of

Table 4 Ecological criteria of PAHs in water and sediment

PAHs	Water (µg/L)	Sediment (µg/g)
naphthalene	490	0.176
acenaphthylene	NA	NA
acenaphthene	23	NA
fluorene	11	0.077
phenanthrene	30	0.042
anthracene	0.3	0.057
fluoranthene	6.16	0.111
pyrene	7	0.053
benzo[a]anthracene	34.6	0.032
chrysene	7	0.057
benzo[b]fluoranthene	NA	NA
benzo[k]fluoranthene	NA	NA
benzo[a]pyrene	0.014	0.032
dibenzo[a,h]anthracene	5	0.033
benzo[ghi]perylene	NA	NA
indeno[1,2,3-cd]pyrene	NA	NA
ΣPAHs	NA	4

NA: not available

that PAHs, HQ is hazard quotient. In principle, $HQ > 1.0$ indicates that the PAHs might pose potential risk to ecosystems, while $HQ < 1.0$ indicates that the risk was relatively lower. The larger HQ ratio means the higher ecological risk.

The concentrations of PAHs in water and sediment were first sorted out and statistically analyzed as mentioned earlier. Some abnormal data, which could not exactly explain the whole PAHs distribution in certain rivers were eliminated. Moreover, the ecological criteria toxicity data of PAHs in fresh water and sediment for the protection of aquatic life were collected from relative literature (Smith et al. 1996; MacDonald et al. 2000; TNRC 2001). Thereafter, PAHs levels with national and international guidelines for the protection of aquatic life were summarized in Table 4. Based on the PAHs exposure concentrations in Chinese rivers discussed above and the toxicity reference values of individual PAHs, the quotients were calculated for each of the 16 PAHs. The results showed that the HQs for 16 individual PAHs in water were less than 1.0 except for anthracene in some sampling sites, i.e., in Liaohe River (mean = 3.2), in rivers from Hangzhou city (mean = 0.7) and in Jiulong River (mean = 2.0). While in sediments, HQs of 6 PAHs, including phenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene and benzo[a]pyrene, were above 1.0. To sum up, the ecological risk of PAHs in Chinese rivers to aquatic organisms was relatively low. Whereas it also could be easily observed that HQs of 7 PAHs, including phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[a]pyrene were

higher than 1.0 in some dissolved phase samples and sediment samples. Therefore, these PAHs were screened as the potential threat to aquatic environment. Further ecological risk assessment of these screened PAHs needs to be carried out in the near future.

Conclusions

PAHs occurred widely in Chinese rivers. In aquatic multimedia, low-ring PAHs were dominant in water and high-ring PAHs were dominant in SPM and in sediment. In general, PAHs concentrations in rivers from the northern China was higher than those from the southern China and highest PAHs concentrations occurred in Liaohe River and in rivers around Tianjin Area, even compared with rivers in the world. Among the 16 PAHs in Chinese rivers, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[a]pyrene were screened using quotient method. These PAHs might have potential ecological risk to aquatic organisms.

Acknowledgements This study was supported by the National Basic Research Program of China (2007CB407304), the National Natural Science Foundation of China (20737003) and Ministry of Environmental Protection (200709034).

References

- Bai YJ, Liu WX, Tao S et al (2007) Distribution of PAHs in surface waters of Hebei Province. *Acta Sci Circumst* 27(8):1364–1369 (in Chinese)
- Brain RA, Sanderson H, Sibley PK et al (2006) Probabilistic ecological hazard assessment: Evaluating pharmaceutical effects on aquatic higher plants as an example. *Ecotox Environ Safe* 64:128–135
- Broman D, Naf C, Rolff C et al (1991) Occurrence and dynamics of polychlorinated dibenzo-p-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of the Baltic. *Environ Sci Technol* 25(11):1850–1864
- Cao Z, Wang Y, Ma Y et al (2005) Occurrence and distribution of polycyclic aromatic hydrocarbons in reclaimed water and surface water of Tianjin, China. *J Hazard Mater* 122:51–59
- Chen B, Xuan X, Zhu L et al (2004) Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. *Water Res* 38:3558–3568
- Chen Y, Zhu L, Zhou R (2007) Characterization and distribution of polycyclic aromatic hydrocarbon in surface water and sediment from Qiantang River, China. *J Hazard Mater* 141:148–155
- Countway RE, Dickhut RM, Canuel EA (2003) Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary. *Org Geochem* 34:209–224
- Doong RA, Lin YT (2004) Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. *Water Res* 38:1733–1744
- Fang MD, Hsieh PC, Ko FC et al (2007) Sources and distribution of polycyclic aromatic hydrocarbons in the sediments of Kaoping river and submarine canyon system, Taiwan. *Mar Pollut Bull* 54:1179–1189
- Feng C, Xia X, Shen Z et al (2007) Distribution and sources of polycyclic aromatic hydrocarbons in Wuhan section of the Yangtze River, China. *Environ Monit Assess* 133:447–458
- Fernandes MB, Sicre MA, Boireau A et al (1997) Polyaromatic hydrocarbon (PAH) distributions in the Seine River and its estuary. *Mar Pollut Bull* 34:857–867
- Fu JM, Mai BX, Sheng GY et al (2003) Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. *Chemosphere* 52:1411–1422
- Gu SH, Kraloveca AC, Christensen ER et al (2003) Source apportionment of PAHs in dated sediments from the Black River, Ohio. *Water Res* 37:2149–2161
- Guo W, He M, Yang Z et al (2007) Distribution of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River watershed, China. *Chemosphere* 68:93–104
- He Y, Yan J (2006) Distribution and ecological risk assessment of PAHs in sediments from Huaihe River. *Ecol Environ* 15(5):949–953 (in Chinese)
- Jiang B, Zheng HL, Huang GQ et al (2007) Characterization and distribution of polycyclic aromatic hydrocarbon in sediments of Haihe River, Tianjin, China. *J Environ Sci* 19:306–311
- Kim GB, Maruya KA, Lee RF et al (1999) Distribution and sources of polycyclic aromatic hydrocarbons in sediments from Kyeonggi Bay, Korea. *Mar Pollut Bull* 38:7–15
- Ko FC, Baker J, Fang MD et al (2007) Composition and distribution of polycyclic aromatic hydrocarbons in the surface sediments from the Susquehanna River. *Chemosphere* 66:277–285
- Li G, Xia X, Yang Z et al (2006) Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environ Pollut* 144:985–993
- Liu M, Baugh PJ, Hutchinson SM et al (2000) Historical record and sources of polycyclic aromatic hydrocarbons in core sediments from the Yangtze Estuary, China. *Environ Pollut* 110:357–365
- Liu Y, Chen L, Zhao J et al (2008) Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. *Environ Pollut* 154:298–305
- Lu JL, Cai B, Hao LB et al (2007) Preliminary study on polycyclic aromatic hydrocarbons in bottom mud from the middle and lower reaches of the second Songhua river. *Rock Miner Anal* 26(4):325–327 (in Chinese)
- Luo X, Mai B, Yang Q et al (2004) Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in South China. *Mar Pollut Bull* 48:1102–1115
- Luo XJ, Chen SJ, Mai BX et al (2006) Polycyclic aromatic hydrocarbons in suspended particulate matter and sediments from the Pearl River Estuary and adjacent coastal areas, China. *Environ Pollut* 139:9–20
- MacDonald DD, Ingersoll CG, Berger TA (2000) Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. *Arch Environ Con Tox* 39:20–31
- Mackay D (2001) Multimedia environmental models: the fugacity approach, 2nd edn. Lewis, Boca Raton, pp 199–201
- Mai B, Fu J, Zhang G et al (2001) Polycyclic aromatic hydrocarbons in sediments from the Pearl river and estuary, China: spatial and temporal distribution and sources. *Appl Geochem* 16:1429–1445
- Manoli E, Samara C (1999) Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *Trends Anal Chem* 18(6):417–428
- Manoli E, Samara C, Konstantinou I et al (2000) Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. *Chemosphere* 41:1845–1855
- Manz M, Wenzel KD, Dietze U et al (2001) Persistent organic pollutants in agricultural soils of central Germany. *Sci Total Environ* 277:187–198

- Maskaoui K, Zhou JL, Hong HS et al (2002) Contamination by polycyclic aromatic hydrocarbons in the Jiulong River Estuary and Western Xiamen Sea, China. *Environ Pollut* 118:109–122
- Means JC, Wood SG, Hassett JJ et al (1980) Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environ Sci Technol* 14(12):1524–1528
- Mitra S, Bianchi TS (2003) A preliminary assessment of polycyclic aromatic hydrocarbon distributions in the lower Mississippi River and Gulf of Mexico. *Mar Chem* 82:273–288
- Mitra S, Dickhut RM (1999) Three-phase modeling of polycyclic aromatic hydrocarbon association with pore-water-dissolved organic carbon. *Environ Tox Chem* 18(6):1144–1148
- Na'f C, Broman D, Pettersen H et al (1992) Flux estimates and pattern recognition of particulate polycyclic aromatic hydrocarbons, polychlorinated dibenzo-p-dioxins, and dibenzofurans in the waters outside various emission sources on the Swedish Baltic coast. *Environ Sci Technol* 26(7):1444–1457
- Nizzetto L, Lohmann R, Gioia R et al (2008) PAHs in air and seawater along a North-South Atlantic transect: trends, processes and possible sources. *Environ Sci Technol* 42(5):1580–1585
- Notar M, Leskovsek H, Faganeli J (2001) Composition, distribution and sources of polycyclic aromatic hydrocarbons in sediments of the Gulf of Trieste, Northern Adriatic Sea. *Mar Pollut Bull* 42(1):36–44
- Qiao M, Wang CX, Huang SB et al (2006) Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. *Environ Int* 32:28–33
- Readman JW, Mantoura RFC, Rhead MM (1984) The physicochemical speciation of polycyclic aromatic hydrocarbons (PAH) in aquatic systems. *J Anal Chem* 319:126–131
- SEPA of China (2004) Tenth-five-year plan of water pollution prevention and control for “Three rivers and three lakes”, 1st edn. Chemical Industry Publishing Company, Beijing
- Shi Z, Tao S, Pan B et al (2005) Contamination of rivers in Tianjin, China by polycyclic aromatic hydrocarbons. *Environ Pollut* 134:97–111
- Smith SL, MacDonald DD, Keenleyside KA (1996) A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *J Great Lakes Res* 22(3):624–638
- Soclo HH, Garrigues PH, Ewald M (2000) Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Mar Pollut Bull* 40(5):387–396
- Solomon K, Giesy J, Jones P (2000) Probabilistic risk assessment of agrochemicals in the environment. *Crop Prot* 19:649–655
- Sun JH, Wang GL, Chai Y et al (2008) Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China. *Ecotoxicol Environ Saf* (in press)
- Tao S, Cao HY, Liu WX et al (2003) Fate modeling of phenanthrene with regional variation in Tianjin, China. *Environ Sci Technol* 37(11):2453–2459
- Tao S, Cui YH, Xu FL et al (2004) Polycyclic aromatic hydrocarbons (PAHs) in agricultural soft and vegetables from Tianjin. *Sci Total Environ* 320(1):11–24
- Tianjin Environmental Protection Bureau (2001) Environmental quality report of Tianjin in 1996–2000
- TNRCC (2001) guidance for conducting ecological risk assessments at remediation sites in Texas. RG-263
- Tolosa I, Mora SD, Sheikholeslami MR et al (2004) Aliphatic and aromatic hydrocarbons in coastal Caspian sea sediments. *Mar Pollut Bull* 48:44–60
- United States Environmental Protection Agency (US EPA) (2008) Method 610: polycyclic aromatic hydrocarbons
- Viguri J, Verde J, Irabien A (2002) Environmental assessment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Santander Bay, Northern Spain. *Chemosphere* 48:157–165
- Wang JZ, Guan YF, Ni HG et al (2007) Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): concentrations, fluxes, and fate. *Environ Sci Technol* 41:5614–5619
- Yang ZF, Feng JL, Niu JF et al (2008) Release of polycyclic aromatic hydrocarbons from Yangtze River sediment cores during periods of simulated resuspension. *Environ Pollut* 155:366–374
- Zakaria MP, Takada H, Tsutsumi S et al (2002) Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs. *Environ Sci Technol* 36:1907–1918
- Zhang ZL, Hong HS, Zhou JL et al (2003) Fate and assessment of persistent organic pollutants in water and sediment from Minjiang River Estuary, Southeast China. *Chemosphere* 52:1423–1430
- Zhang Z, Huang J, Yu G et al (2004) Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. *Environ Pollut* 130:249–261
- Zhang YX, Tao S, Cao J et al (2007) Emission of polycyclic aromatic hydrocarbons in China by county. *Environ Sci Technol* 41:683–687
- Zhou JL, Maskaoui K (2003) Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. *Environ Pollut* 121:269–281
- Zhu LZ, Chen BL, Wang J (2004) Pollution survey of polycyclic aromatic hydrocarbons in surface water of Hangzhou, China. *Chemosphere* 56:1085–1095