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Chapter 5

Pollution of Polycyclic Aromatic Hydrocarbons in China

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Abstract

With its rapid economic growth, China is encountering serious environmental problems. As the result of a sharp increase in energy consumption in the past 20 years, large quantities of polycyclic aromatic hydrocarbons (PAHs) were released into the environment. PAH concentrations in the atmosphere, water, and soil were increasing year by year. Because the Chinese government had financed many research programmes on the investigation of environmental pollution with PAHs, basic understanding of the pollution patterns and pollution sources of PAHs in China was achieved. In this paper, PAH pollution in the atmosphere, water and sediment, and soil and plants was reviewed. Comparisons of literature values of PAHs in China and those of western countries show that PAH pollution in China is more serious than in other countries. PAHs concentrations in atmosphere, water, sediment and soil in China were in the range of $60–2900\,\mathrm{ng\,m^{-3}}$, $1–98\,\mu\mathrm{g\,l^{-1}}$, and $0.005–182\,\mu\mathrm{g\,g^{-1}}$, respectively. The identification of sources of PAHs in different environmental media revealed that atmospheric PAHs come from primarily coal combustion and petrogenic sources; and water and soil PAH pollution from atmospheric deposition, industrial wastewater discharge, and wastewater irrigation. The environmental pollution of PAHs in water and soil also caused the bioaccumulation of PAHs in fish, bivalves, vegetables and agriculture plants. The human health risks of PAH pollution in China need to be more extensively investigated in the future.

5.1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants (POPs) and widespread environmental contaminants, some of which may exhibit toxic, carcinogenic and mutagenic effects Because of their low water solubility and hydrophobic nature, PAHs are partitioned

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strongly into nonaquatic phases. They tend to be associated with particulates and are widely transported through atmospheric routes. PAHs have been detected throughout the environment (i.e., aerosol, soil, water, sludge and sediment). There has been a worldwide increase in interest in PAHs. Sixteen individual PAHs have been identified as priority pollutants by the United States Environmental Protection Agency (USEPA).

PAH contamination not only reduces the quantity and quality of natural resources, but may also have a deleterious impact on wildlife. Low molecular weight PAHs that have 2 or 3 rings, such as naphthalene, methylnaphthalene, and acenaphthene, are acutely toxic but noncarcinogenic to a broad spectrum of organisms. On the other hand, high molecular weight (HMW) PAHs that have 4, 5, or 6 rings, such as flouranthene, pyrene, benzo[*a*]pyrene, chrysene, and benzo[*g*,*h*,*i*]perylene, are less acutely toxic but have greater carcinogenic potential (Kennish, 1996). Once they enter the atmosphere, PAHs are distributed between gas and particle phases and subject to removal mechanisms, such as oxidative and photolytic reactions and wet and dry deposition (Garban et al., 2002). Low molecular weight PAHs are found mostly in the gas phase, whereas high molecular weight PAHs are typically associated with airborne particles (Gundel et al., 1995; Lighty et al., 2000).

PAHs enter the environment from both natural and man-made sources, and the anthropogenic point and nonpoint sources are the major sources. The nonpoint sources are diffuse sources disseminated through the air and waterways. In aquatic systems, PAH-enriched particles or flocs may settle to the lake's bottom under calm conditions and accumulate in the sediments. Once the PAH-enriched particles have accumulated in the lake's floor, they may undergo a number of changes that are mediated by chemical or microbial activities. As a result, the bound PAHs can be released from the sediment into the water phase. Once they enter the water column, they may also enter phytoplankton. The PAHs in phytoplankton may then bioaccumulate in the food web. This can cause both acute and chronic effects in fish, birds and other mammals that feed on aquatic organisms (Zhang, 1998).

5.2. PAHs in the atmosphere

5.2.1. Distribution and transportation of PAHs in the atmosphere

PAHs are semi-volatile organic compounds that are persistent in atmosphere, both in gas phase and particles. Much work has been done about the seasonal variation, vertical distribution and particle size distribution of PAHs in the atmosphere. In China, research on PAHs has been conducted since the 1980s. The concentrations of PAHs in the air have been investigated in several cities, especially those in northern China. Table 5.1 shows the total PAH and benzo[*a*]pyrene concentrations reported in literature, comparing the levels of PAHs in several Chinese cities. Most of these studies focused on aerosol PAHs at ground level in different seasons or in different function zones. Other studies involved PAHs in the gas phase, at higher altitude, or in indoor airborne particles. Though the sampling conditions and analytical procedures (e.g., sampling height, number of PAHs, etc.) of these studies were different, this comparison reveals meaningful basic information about PAH distribution in cities of China.

The data shown in Table 5.1 indicate that the atmospheric concentrations of PAHs vary largely in cities despite the different sampling conditions. In cities north of the Changjiang (Yangtze) River, coal-fueled space-heating systems are usually utilized, accounting for a large contribution of particles and PAHs in the atmosphere. The ΣPAHs in the winter in Taiyuan, Tianjin, and Lanzhou were 1703 (ΣPAHs9, sum of 9 PAHs, Peng & Zhang, 2000), 465 (ΣPAHs10, Zhu et al., 1998) and 1077 ng m^{-3} (ΣPAHs16, Peng et al., 2000), respectively. In the southern cities, the ΣPAHs16 in the winter was 146 (Liuzhou) (He et al., 2005) and the ΣPAHs10 in Hengyang was 127 ng m^{-3} (winter) (Li et al., 2004). In the summer, the differences of total PAH concentrations were smaller than those in winter, as 596 ng m^{-3} in Lanzhou (ΣPAHs16, Peng et al., 2000) and 141 ng m^{-3} in Hengyang (ΣPAHs10, Li et al., 2004). Although these values involve different numbers of PAHs, the most abundant ones, such as phenanthrene and benzo[*a*]pyrene were included in all the investigations. Thus, the total PAH concentrations summarized in Table 5.1 can be ranked. Benzeno[*a*]pyrene (BaP) was monitored in all the studies due to its strong carcinogencity and severe public health concerns. Average BaP concentrations shown in Table 5.1, except the concentrations in Hengyang and Liuzhou (spring), are all higher than 10 ng m^{-3}, the China National Atmospheric Environmental Standard. Several data were even higher than 30 ng m^{-3}. The observations suggest considerable differences in the levels of PAH pollution among Chinese cities.

In the same city, the distribution patterns of PAHs were examined in four interactive main aspects: PAHs composition, spatial distribution, seasonal variation, gas phase and particle size distribution and vertical distribution.

Table 5.1. Some PAH concentrations in airborne particles in cities of China (the data were obtained from aerosol samples at ground level if without specific explanation)

City	Region function	Concentrations ($ng\,m^{-3}$)			Sampling time	Literature
		ΣPAHs	No. of PAHs	BaP		
Taiyuan	Industry	2020.4	9	91.0	February 1998 (heating)	Peng and Zhang (2000)
	Chemical industry	2898.0		119.3		
	Downtown	1052.1		56.4		
	Residential region	843.6		32.0		
	Average	1703.5		74.7		
Tianjin	Downtown	465.4	10	465.4	November 1994 (heating)	Zhu et al. (1998)
	Petrochemical industry	173.1		13.6		
Liuzhou	Average	145.7	16	19.19	December 2002 (no heating)	He et al. (2005)
					January 2003 (no heating)	
		59.9		4.72	February 2003 (no heating)	
					March 2002 (no heating)	
Lanzhou	Chemical industry	1604.4	16	64.4	March 1996 (heating)	Peng et al. (2000)
	Residential area	1640.6		113.9		
	Traffic area	653.3		59.5		
	Rural area	411.2		22.6		
	Average	1077.4		65.1		
	Chemical industry	1501.7		87.0	July 1996 (no heating)	
	Residential area	376.8		25.8		
	Traffic area	233.2		9.4		
	Rural area	270.3		–		
	Average	595.5		30.6		
Hengyang	Average	140.7	10	6.29	July 2002 (no heating)	Li et al. (2004)
	Average	127.0		7.27	February 2003 (no heating)	
Beijing		107.49		5.85	Four seasons, 2003	Zhou et al. (2005)

5.2.1.1. Composition

The composition of PAHs is mainly influenced by the source as well as degradation. Different sources contain PAHs with distinct composition. Because PAHs with low degradability usually exist longer than those with high degradability, the composition of PAHs in samples can reveal source and aging information.

Zhou et al. (2005) have reported the composition of atmospheric PAHs in Beijing. Lower molecular weight (2–3 rings) PAHs were less than 15% of the total mass (except in urban summer sample), while heavier PAHs (4 rings and more) showed three distribution patterns: spring type, summer type, and autumn and winter type.

Spring type: the normalized concentration of PAHs increased with molecular size. 6-ring benzo[*g*,*h*,*i*]perylene, indeno[1,2,3-*cd*]pyrene, and 5-ring benzo[$b+k$] fluoranthene accounted for the majority of the total PAH concentrations, indicating that traffic emission was clearly a significant source of PAHs in spring.

Summer type: the distribution characteristic of PAHs varied greatly in two sites. Four-ring fluoranthene, pyrene, and 3-ring phenanthrene dominated the total PAHs in urban sampling site, and BeP/BaP ratio was 2.17, resembling the PAH source fingerprints for diesel engines (Rogge, 1993). These distribution characteristics were presumably related to emission of diesel-fueled, heavy-duty trucks in the nighttime. Meanwhile, 6-ring benzo[*g*,*h*,*i*]perylene, 5-ring benzo[$b+k$]fluoranthene and benzo[*e*]pyrene were the most abundant in suburban samples.

Autumn + winter type: 4-ring PAHs were found to be the most abundant; floranthene, pyrene, benzo[*a*]anthracene, and chrysene accounted for more than 50% of the total PAHs. The likely sources are coal combustion and vehicle exhaust.

5.2.1.2. Spatial distribution

Spatial distribution is mainly attributed to the differences in emission patterns, meteorological conditions and local topography of distinct city functional areas. Many studies have examined the effects of these differences.

Zheng et al. (1997) have reported the total concentration of PAHs in Hong Kong in the winter months of 1993. These concentrations ranged from 2.4 to 54 ng m^{-3}. In this study, the highest value of BaP (1.07 ng m^{-3}) was found in Mong Kok site (commercial, residential and traffic environment) and the lowest (0.03 ng m^{-3}) in Hok Tsui (rural and marine environment), suggesting that the Mong Kok site, located near streets in one of the busiest districts of Hong Kong, was heavily influenced by traffic.

Guo et al. (2003a) also studied PAH spatial distribution in 2000–2001 in Hong Kong. The two sampling sites were Hung Hom (PU) and Kwun Tong (KT). The former is adjacent to a road with very high traffic volumes and the latter lays in a commercial, industrial and residential area. The mean concentrations of individual PAHs in the aerosols at the PU site were much higher than those at the KT site, especially in winter. The total PAH concentrations in $PM_{2.5}$ and in PM_{10} at PU site were $\sim$1.25 and 1.45 times that at KT site, respectively. The major cause of the difference was the distinct characteristics of sampling sites. It is well known that PAHs are major components of vehicle exhaust, especially gasoline and diesel-powered vehicles (Miguel et al., 1998). Traffic influenced the PU site severely. The major sources of PAHs at KT site were household cooking activities, industrial sources and vehicle emissions. However, the source strength of PAHs at this site was much lower than that at PU site, because the traffic volume was much lower and the sampling site was far from the ground level. PAHs, whether released by anthropogenic or biogenic processes, have their primary sources near the surface and are lost as they are transported from the surface to the boundary layer (Goldan et al., 2000).

A similar pattern was obtained from the PAH concentrations at four functional zones in Liuzhou (He et al., 2005). The highest total PAH concentrations were observed at the sampling site south of an industrial zone during winter and spring, when the north wind dominates in Liuzhou. The main source of PAHs in Liuzhou was industrial fuel combustion, suggesting that the meteorological conditions affect the distribution and transportation of PAHs greatly.

Studies conducted in Macao (Qi et al., 2000) showed that the PAH concentrations of commercial and traffic zones were higher than that of relatively cleaner function zones.

In the northern cities, the results may be quite different from those in the south such as Hong Kong and Liuzhou. In the north, coal- and petrol-fueled space-heating systems are widely used in winter in residential areas, and coal and petrol are also the energy source and materials of several important industries. Thus, coal and petrol combustion, as opposed to traffic emission, contributes most of the PAHs in the atmosphere, as demonstrated in some studies.

Zhu et al. (1998) have investigated the PAH concentrations in airborne particles in Tianjin. Four sampling sites were set at Dagang, a petrochemical industry zone. A sampling site in downtown was used as a control. Results showed that the sum of 10 PAHs in the Dagang petrochemical industry zone ($168.8\,ng\,m^{-3}$) was lower than that in Tianjin downtown ($465.4\,ng\,m^{-3}$). The concentration of BaP was lower in Dagang as well ($13.6\,ng\,m^{-3}$ in Dagang and $41.4\,ng\,m^{-3}$ in downtown).

However, an opposite result was obtained by Peng et al. (2000). This study investigated the distribution and sources of PAHs in airborne particles in Taiyuan. The results showed that the mean concentration of the sum of nine PAHs was 189.2 ng m^{-3}, and the mean concentration of BaP was 74.7 ng m^{-3}. The concentration changed with function zones: chemical industrial zone > industrial zone > commercial and dwelling zone > cultural zone. The concentrations of 16 PAHs in airborne particles in the different function zones of the city of Lanzhou showed a different pattern: chemical industry zone > commercial zone > traffic zone > suburban zone (Peng et al., 2000) The difference in the spatial distribution was possibly due to the local emission patterns and meteorological conditions.

Zhou et al. (2005) have reported the spatial distribution of PAHs in atmospheric PM_{10} in Beijing. 17 PAHs were quantified in samples collected at 15 m high in urban and suburban areas. Individual concentrations between 0.01 and 55.2 ng m^{-3} were found and the total PAH concentrations varied from 8.6 to 297 ng m^{-3} with an average of 107 ng m^{-3}. PAH concentrations in the urban site were 1.02~1.58 times higher than those measured in the suburban site.

5.2.1.3. Seasonal variation

The seasonal distribution of particle-associated PAHs is controlled by a combination of emission factors (EFs), dispersion conditions and chemical mechanisms (Caricchia et al., 1999; Menichini et al., 1999). This balance depends on the relative importance of degradation processes and emission sources (Guo et al., 2003b). The highest PAH concentrations of a sampling site were usually obtained from winter samples, and the differences were far higher in northern cities than southern ones, suggesting that coal combustion for space heating contributes the most PAHs in winter in Northern China.

PAHs in total suspended particle samples collected in Qingdao during June 2001–May 2002 were analyzed by Guo et al. (2003b). The total concentrations ranged from 2.2 (summer) to 240.5 ng m^{-3} (winter). The annual average was 87.5 ng m^{-3} and the seasonal averages were 12.3, 28.0, 177.2 and 13.1 ng m^{-3}, respectively for summer, fall, winter and spring. The lowest concentration of total PAHs was found in the summer samples followed by the spring and fall samples while the highest was observed in the winter samples. The concentration of PAHs was 14.4 times higher in winter than in summer. The seasonal variations were mainly due to seasonal energy profiles. Other studies showed that the changes in emission patterns (stationary and vehicular) and meteorological conditions (including fewer daylight hours, reduced ambient temperatures, and lower volatilization and photochemical activity) contributed to the higher PAH levels during the winter (Bjorseth & Ramdahl, 1985; Freeman & Cattlel, 1990; Baek et al., 1991).

Guo et al. (2003a) has observed higher PAH concentrations in the winter and lower concentrations in the summer in Hong Kong. The total PAHs ratio of winter to summer was 8.6 at PU site and 7.5 at KT site, respectively. The ratios at the PU and KT sites were in accordance with results reported by other studies in Europe and in the USA: PAHs in the winter were generally higher by a factor of 1.5–10 than those in the summer (Baek et al., 1991; Harrison et al., 1996; Caricchia et al., 1999; Menichini et al., 1999). In Hong Kong, there is little seasonal variation in emissions from stationary sources since space heating is unnecessary. Thus, the higher PAH concentration in the winter was probably due to the contribution of outside sources. It is known that in winter the prevailing wind in Hong Kong is northeasterly, which brings in highly polluted air masses from the mainland to the sampling sites. On the contrary, in the summer, the Asian monsoon brings in clean oceanic air from the Tropics and unstable rainy weather. Thus, lower PAH levels were likely attributed to the combination of easier atmospheric dispersion of pollutants, washout effects, and to a lesser extent, photo degradation and higher percentage in the air in the vapor phase.

5.2.1.4. Diurnal variation

In some areas, the main source of PAHs is domestic emission from inhabitant activities. Thus, the distribution of PAHs may vary during the daytime and nighttime. This has been confirmed by some studies.

Qi et al. (2000) has reported that in Macao, the PAH concentrations during the daytime were generally 1.24–4.17 times higher than those during the nighttime at the same sampling site.

5.2.1.5. Vapor and particle phase distribution

PAHs can be further categorized as low and high molecular weight types (LMW and HMW) since the distribution and transport patterns of the two groups are distinct due to vapor pressure differences.

Guo et al. (2003b) observed that the winter and spring LMW and HMW were almost equally split (45.0 and 44.4%, respectively), while in the summer, the HMW PAHs dominated (72.0%). The difference in distribution was due to the gas-particle partitioning of these compounds in the atmosphere (Bidleman et al., 1986; Zheng & Fang, 2000; Zheng et al., 2000).

5.2.1.6. Vertical distribution

Because the construction of high-rises has become popular in urban residential areas in China in recent years, it is important to evaluate the vertical distributions of airborne pollutants to reveal the respiring exposure of residential population within those high buildings (Li et al., 2005).

In the study of Li et al. (2005), results showed clearly that there is a significant decrease in the concentrations of PAHs accompanied an increase in the height above the ground level. However, the decrease slowed down at the height of 24 m for PAHs, probably due to the existence of a quasi-equilibrium state at this height where the dilution and transformation processes of vehicular exhaust plume have already taken place. In addition, the trends for 4-through 7-ring PAHs at different heights were very similar.

Similarly, it was found that the level of PAHs measured at 25 m decreased to 30–50% of that measured at ground level (Bi et al., 2005).

5.2.1.7. Indoor and outdoor distribution

Indoor air pollution is a major global public health threat requiring greatly increased efforts in the area of research and policymaking, because people spend more than 80% of their time indoors, mostly in their homes (Li et al., 2005). The relationship between indoor and outdoor PAH concentrations is also an important part of the PAH distribution pattern. The results varied in the cities because of their different emission and ventilation patterns.

The study of Li et al. (2005) was conducted in Guangzhou, where direct air exchange between indoor and outdoor is common due to open doors and windows all year round with no residential heating. The total PAH concentrations ranged from 15.8 to 84.8 $\mathrm{ng\,m^{-3}}$ and from 14.2 to 77.9 $\mathrm{ng\,m^{-3}}$ in the outdoor and indoor samples, respectively. The contribution profiles of all individual PAHs were very similar in the indoor and outdoor samples, with 5–7-ring PAHs as the predominant contributors (79–90%). The indoor/outdoor (I/O) ratio, which is usually used to describe the I/O relationships of air pollutants for individual PAHs, was close to 1 (0.93–1.09), indicating that indoor concentrations of PAHs were dominated by outdoor sources.

5.2.1.8. Phase and particle size distribution

Once PAHs enter the atmosphere, they are distributed between gas and particle phases and subject to removal mechanisms, such as oxidative and photolytic reactions, as well as wet and dry deposition (Garban et al., 2002). The transport, deposition and chemical transformations of PAHs and other semi-volatile organic compounds are extensively controlled by their gas/particle-phase partitioning (Bi et al., 2005; Wu et al., 2005). Therefore, phase partitioning plays an important role in spatial distribution and transport. Low molecular weight PAHs (2–3-ring PAHs) are found mostly in the gas phase, whereas high molecular weight PAHs (4–6-ring PAHs) are typically associated with airborne particles (Gundel et al., 1995; Lighty et al., 2000).

Bi et al. (2005) measured 37 PAHs in both particulate and vapor phase samples. The average concentrations were in the range of 134.4–298.5 ng m^{-3} in the Liwan district of Guangzhou. Results showed that the mass distribution in air (including vapor and particulate phase) was dominated by phenanthrene, methylphenanthrene, fluoranthene, pyrene, chrysene, indeno[1,2,3-*cd*]pyrene and benzo[*g*,*h*,*i*]perylene, which together accounted for 69 and 77% of the total in samples from ground level sites and 25 m high level sites, respectively. Higher concentrations of low molecular weight compounds such as phenanthrene, fluoranthene and pyrene occurred in July vapor phase samples, exhibiting a positive correlation with air temperature, while the concentrations of HMW compounds, such as benzofluoranthene and benzopyrene, were negatively correlated with temperature. Higher concentration in particulate phase was present in April. The particle phase fraction ranged from 9.4% of the total PAHs in July to 44.8% in April. PAHs belong to the semi-volatile organic contaminant class and occur in both gaseous and particulate phases in the atmosphere. The vapor-particle partition exhibits a strong dependence on molecular weight. LMW PAHs tend to have a higher concentration in the vapor phase while HMW ones are often associated with the particles. The vapor-phase PAH chromatograms are characterized by strong peaks of congeners with 3–4 rings, of which fluorine, phenanthrene and their methylated derivatives, fluoranthene, and pyrene are the dominant PAH species, while HMW (>252) PAHs species were not detected in the vapor phase due to their low volatility. Higher molecular weight PAHs, from chrysene to coronen except perylene, dominated PAHs in the particulate phase with benzo[*g*,*h*,*i*]perylene as the highest.

Another study (Guo et al., 2003a) showed that the sum of 16 PAHs in PM_{10} was higher than that in $PM_{2.5}$ at two sites in the same season. For instance, at the PU site, in the summer, the total PAH concentration in $PM_{2.5}$ was 4.87 ng m^{-3} while in PM_{10} it was 5.82 ng m^{-3} (Table 5.1). At the KT site in the winter, the sum of PAHs in $PM_{2.5}$ was 27.9 ng m^{-3} and PAHs in PM_{10} was 38.6 ng m^{-3}. For individual PAHs, most at these two sites had similar patterns to $PM_{2.5}$ and PM_{10} except for benzo[*a*]pyrene and benzo[*k*] fluoranthene. The results indicate that most of the PAHs are in the $PM_{2.5}$ fraction. There was no statistical difference in ratios for individual PAHs in either season at the two sites. This reflects that the ratios of individual PAHs in $PM_{2.5}$ to that in PM_{10} in Hong Kong have common patterns, regardless of speciation, season and sampling locations.

5.2.1.9. Transport

Airborne particles may be delivered to surfaces by wet and dry deposition. Several transport mechanisms, such as turbulent diffusion, precipitation, sedimentation, Brownian diffusion, interception, and inertial migration, influence the dry deposition process of airborne particles. Large particles (dN10Am) are transported mainly by sedimentation; hence, large particulate PAHs tend to be deposited nearer the sources of emission Small particles (db1Am), which behave like gases, are often transported and deposited far from where they originated (Baek et al., 1991; Wu et al., 2005).

The transport pathway is severely influenced by meteorological conditions. In some northern cities, such as Tianjin, the dry deposition of airborne PAHs is highly likely to be the predominant mode of atmospheric loading to underlying surfaces (Wu et al., 2005). Wu et al. (2005) have studied the PAHs in dustfall in Tianjin; the total amount of PAH16 (sum of 16 PAH compounds) in the dustfall ranged from 1.0 to $48.2\,ng\,g^{-1}$ with a mean of $6.6\,ng\,g^{-1}$ for the nonheating season, and from 2.5 to $85.5\,ng\,g^{-1}$ with a mean of $10.7\,ng\,g^{-1}$ for the heating season. The profiles of the PAH compounds in the samples collected in different seasons are similar. The dominant species in the heating season were naphthalene, phenanthrene, fluoranthene, and chrysene in dustfall and naphthalene, fluorine, phenathrene and fluoranthene during the nonheating season. This corresponds to 79 and 76% of total PAH concentrations for heating and nonheating seasons, respectively. The concentrations of most individual PAH compounds in the heating season samples were higher than those in the nonheating season samples with the exceptions of acenaphthene, fluorine and fluoranthene. It should be emphasized, however, that these are general trends. The fractions of HMW PAHs (4–6 rings) in the bulk of the dustfall samples from the heating season were higher than those from the nonheating season except for samples collected from an industrial area in eastern Tianjin and those collected from locations near open coal storage sites and traffic roads. Seasonal variation in the ΣPAH456 values (sum of 4–6-ring PAHs) reflects the increase in fossil fuel consumption in winter. The deposition was highest in urban and east industrial areas during the heating season. Compared with those of the nonheating season, samples from the heating season were characterized by a higher fraction of high molecular weight PAHs with 4–6 rings, except for those from the east industrial area. The east industrial area had more significant correlations between individual PAH compounds, and more discrete triangular components of 3-, 4-, 5-, and 6-ring PAHs. The deposition fluxes of ΣPAH15 (sum of 15 PAHs except naphthalene), ΣPAH6 (sum of 6 carcinogenic PAHs recommended by IARC) and benzo[*a*]pyrene (BaP) from atmospheric deposition to the whole area were estimated to be 1911, 196 and 53 $\mathrm{ng\,m^{-2}}$ per year, respectively. Furthermore, the deposition contribution of PAHs during domestic heating season in winter was not significant relative to the annual inputs.

Qingdao is a coastal city in Shandong Province located down wind of the origin (Inner Mongolia and Hebei Province) of the Asian dust storms, which often occur in the spring, when northwesterly winds prevail. Guo et al. (2003b) measured PAHs in dust episodes in Qingdao. Results showed that the average level of PAHs in the Asian dust storm samples (52.8 $\mathrm{ng\,m^{-3}}$) was higher than in the spring samples (13.1 $\mathrm{ng\,m^{-3}}$) but lower than in the winter samples (177.2 $\mathrm{ng\,m^{-3}}$). The ratio of individual PAHs in dust storm samples was the same as that in the spring samples, suggesting that the contribution of PAHs by the storm was insignificant.

Since the weather in the sub-tropical coast region of China is under the influence of the Asian monsoonal circulation, the northwest wind is predominant in the autumn and winter seasons, which may bring the PAHs emitted into atmosphere in the northern cities to the south. Hong Kong may act as a receptor of the huge anthropogenic emissions from this region by long- and medium-range transport, especially in winter (Guo et al., 2003a).

5.2.2. Factors affecting emissions of PAH

5.2.2.1. Source temperature

Source temperature plays an important role in PAH formation. The composition of PAHs varies depending on the combustion temperature. At low to moderate temperatures, such as in a wood stove, or from the combustion of coal, low molecular weight parent PAH compounds are abundant, and display a higher degree of alkylation. On the other hand, at high temperatures, such as in vehicle emissions, HMW parent PAH compounds are dominant, and display a higher number of unsubstituted species. As a result, nonalkylated/alkylated indices are high for pyrogenic PAH mixtures and low for petrogenic PAHs.

5.2.2.2. The rank of coal

The rank of coal (maturity) is an important factor that affects PAH emissions from residential combustion. PAH emission from various coals is found to have a relationship with their volatile contents, and the complete combustion of coals with a high volatile content is more difficult to achieve. Bituminous and sub-bituminous coals with high volatile content yield more PAHs when burned at low temperatures, such as residential combustion, while anthracite coal containing very little volatile matter can burn more completely and emit PAHs with a mass that is three orders of magnitude lower than bituminous coal. Smoky coal, which is burned as fuel for cooking and heating in unvented homes, produces combustion emissions composed primarily of parent PAHs and alkylated PAHs.

5.2.2.3. Burning conditions

Burning conditions also affect PAH emissions. For example, although most of the power plant fuels are bituminous coals, large-scale combustors such as power plants have very low PAH EFs, which are in the same order or even lower than that from anthracite in residential combustion. The poor air supply in residential burning may be another reason for the high production of PAHs. Ledesma et al. (2000) concluded that most of the PAH mass is produced when the oxygen ratio is under 30% during bituminous coal burning. This result indicates that it may be possible to decrease EFs by improving aeration conditions in residential combustion.

In cooking practice, Zhu and Wang (2003) found that during three different cooking practices (boiling, broiling and frying), boiling produced the least levels of PAHs. For fish, a low-fat food, frying it produced a larger amount of PAHs compared to broiling practice, except for pyrene and anthracene. Meanwhile, the production of PAHs from three common cooking oils (lard, rapeseed oil and soybean oil), lard produced more PAHs than rapeseed oil and soybean oil Additionally, an increase in cooking temperature generally increased the production of most PAHs.

5.2.2.4. Other factors

Other factors affecting the emission of PAHs include changes in emission patterns (stationary and vehicular) and meteorological conditions (daylight hours, ambient temperatures and pressure), which affect the volatilization and photochemical activity of PAHs. Zhu and Wang (2005) found that compared to those from gasoline engines, emissions from diesel engines were less toxic, although they might produce more PAHs. Of the same vehicular and oil type, automobiles with longer mileages produced more toxic PAHs. PAH distributions in the vehicular exhausts were related to the oil type. Large difference was found in the relative abundance of 3-, 5- and 6-ring PAHs between exhausts from gasoline and diesel oil engines. Diesel oil engines produced relatively lighter PAHs such as naphthalene, acenaphthene, and fluorine, while gasoline engines emitted heavier kinds such as benzo[*k*]flouranthene, indene and benzo[*g*,*h*,*i*]perylene. The automobile produced more PAHs with the increase of mileage, especially fluorine, pyrene, benzo[*a*]pyrene and benzo[*g*,*h*,*i*]perylene.

5.2.3. Identification of sources

The mixture of PAHs present in a particular sample in many cases mirrors the sources that produce them. Several methods can be used to qualitatively identify the probable sources of PAHs. Commonly used methods include the abundance ratios of individual compounds, the fossil fuel pollution index (FFPI), and diagnostic ratios indicative of sources (petrogenic vs. pyrogenic). Quantitative apportionment of sources needs sophisticated statistical approaches such as the chemical mass balance models (Li et al., 2003).

5.2.3.1. Abundance ratios of individual compounds

5.2.3.1.1. Phenanthrene/anthracene (Ph/An) and fluoranthene/pyrene (Fl/Pyr)

PAHs from different pollution sources have different compositions and relative ratios that can be used as indicators of pollution sources. Ph/An and Fl/Pyr ratios are most commonly used as clues to source and delivery routes of the PAHs (Okonkwo, 1997). The ratio of Ph/An within the 3-ring PAH group and Fl/Pyr within 4-ring PAH group were used to differentiate PAHs of different origins. Phenanthrene is more thermochemically stable than anthracene, and therefore at low maturation temperatures, much higher molar fraction of phenanthrene is produced compared to anthracene. The molar ratios of Ph/An at petroleum maturation temperatures lead to higher values. The ratios could be as high as 50 at 373 K. On the contrary, high temperature processes (800–1000 K), such as the incomplete combustion of organic materials (coal burning, wood burning, vehicular exhaust emission, waste crankcase oil, and asphalt roofing material), are characterized by low Ph/An ratio value.

Therefore, $Ph/An > 15$ may point to petrogenic sources and $Ph/An < 10$ to pyrolytic sources. Due to the wide range of values for this index found in the literature, values between 10 and 15 are considered indeterminate relative to source. In petroleum-derived PAHs, pyrene is more abundant than fluoranthene, while at higher combustion temperatures a predominance of fluoranthene over pyrene is characteristic. So the Fl/Pyr values greater than 1 are obviously related to pyrolytic sources, whereas values less than 1 are attributed to petrogenic sources. In order to avoid erroneous conclusions, the two ratios are often combined. When $Ph/An > 15$ and $Fl/Pyr < 1$, the PAH input is mainly from crude oil sources; and when $Ph/An < 10$ and $Fl/Pyr > 1$, the major input may be related to combustion (Wang et al., 2004b).

5.2.3.1.2. *Methylphenanthrenes/phenanthrene (MP/P)*

The ratio of alkylated PAH homologs to parent compounds is also characteristic of PAH sources. Generally, PAHs from a petrogenic source have LMWs with the depletion of those having HMW, while pyrogenic sources are abundant in HMW PAHs (Zakaria et al., 2002). Petrogenic PAHs are mainly alkylated homologs while pyrogenic are mainly parent PAHs (especially fluoranthene, pyrene). The methylphenanthrenes to phenanthrene (MP/P) ratio is widely used to express the abundance of alkyl homologs and to distinguish petrogenic from pyrogenic sources (Zakaria et al., 2002; Mai et al., 2003). MP/P ratios measured in combustion mixtures are generally lower than 1, whereas those in unburned fossil fuel PAH mixtures typically range from 2 to 6 (Zakaria et al., 2002).

5.2.3.1.3. *Perylene to ΣPAH (PER/ΣPAH)*

In most cases, identifying specific pollutant sources from complicated routes is a great challenge. Generally, in coastal areas, PAH congeners are divided into three categories: petrogenic, pyrogenic and biogenic, based upon diagnostic ratios or composition distributions of parental PAH compounds. Some PAHs, such as perylene, are derived from the diagenetic transformation of terrestrial precursors in the aquatic environment, and partially from petroleum or pyrolytic processes. Their concentrations have been found to vary dramatically from 100 to 4000 ng g^{-1} in marine and estuarine sediments (Venkatesan, 1988). Typically, for pyrogenic PAHs, perylene represents ~1–4% of the ΣPAH concentration (Wakeham et al., 1980; Wang et al., 1999). It has also been suggested that a concentration of perylene higher than 10% of the total pentaaromatics isomers can indicate a probable diagenetic input; if not, then a probable pyrogenic origin. In a study of core samples of four lake sediments, Wakeham et al. (1980) found perylene was usually the most abundant PAH, accounting for 70–90% of the ΣPAH concentration in deeper, older sediment layers where decreasingly anthropogenic PAHs were found.

5.2.3.1.4. Other ratios

Certain diagnostic ratios of alkylated dibenzothiophene and alkylated phenanthrene compounds were used to identify oil incineration residues. Furthermore, two ratios of dibenzothiophene and phenanthrene alkylated homologs, double ratios, were used to distinguish between Ixtoc-1 and non-Ixtoc-petroleum (Boehm et al., 1997). Page et al. (1996) also used double ratios to distinguish background petroleum hydrocarbons from the Exxon Valdez spill oil. Fang et al. (2003) found that the 4,6-dimethyldibenzothiophene/3,6-dimethyl-phenanthrene (4,6-C_2D/3,6-C_2P) ratio was more useful than the MP/P ratio in tracing petrogenic PAHs from the inner harbor area to the adjacent coastal environment.

These ratios should be used in combination to avoid erroneous conclusions regarding origins of PAHs. For example, Lake et al. (1979) found that used motor oil exhibits Ph/An ratios as low as 3, which could easily be misinterpreted as a pyrogenic. Generally, in contrast to pyrogenic sources, petrogenic sources are characterized by high ratios of Ph/An ($\mathrm{Ph/An} > 15$) and MP/P ($\mathrm{MP/P} > 2$) in association with lower ratios of Fl/Pyr ($\mathrm{Fl/Pyr} < 1$) and benzo[*a*]anthracene/chrysene ($\mathrm{BaA/Chr} \leqslant 0.4$) (Readman et al., 2002). Fl/Pyr and BaA/Chr ratios are not sensitive enough to be used to distinguish petrogenic PAHs from pyrogenic PAHs in an area where pollutants come from multiple sources.

5.2.3.2. Fossil fuel pollution index (FFPI)

The FFPI is a diagnostic ratio designed to determine the approximate percentage of fossil fuel PAHs relative to the total PAH in a sample. The FFPI is calculated as:

$$\mathrm{FFPI} = \left[\frac{N\mathrm{s} + P\mathrm{s} + 0.5(P\mathrm{s} + C_1P) + D\mathrm{s}}{\sum \mathrm{PAH}}\right] \times 100,$$

where Ns, Ps and Ds are the sum of the naphthalene, phenanthrene and dibenzothiophene homolog series, respectively. These homolog series include the parent compound and the alkyl-substituted homologs. C_1P is methyl phenanthrene and ΣPAH is the sum of the 2–6-ring PAHs (Savinov et al., 2000).

5.2.3.3. Diagnostic ratios indicative of sources

The combustion/pyrolysis of fossil fuels yields PAH mixtures in which unsubstituted compounds in the higher molecular weight (MW) range

(MW > 178) prevail. PAHs in either fossil fuels or unburned fossil fuel residues are characterized by higher proportions of LMH PAHs and an increased abundance of alkylated homologs.

A concentration ratio of anthracene to the sum of anthracene and phenanthrene, An/(An + Ph) lower than 0.10 is usually taken as an indication of petroleum combustion and a ratio higher than 0.10 as dominance of heavy fuel combustion. Among PAHs with molecular mass of 228, the ratio of benzo[*a*]anthracene to the sum of benzo[*a*]anthracene and chrysene, BaA/(BaA + Chr) is also indicative of the sources. A ratio lower than 0.20 suggests a petroleum source, whereas a ratio from 0.20 to 0.35 indicates either a petroleum or combustion source, and any ratio higher than 0.35 signify a combustion origin. Similarly, petroleum sources may be suggested by a ratio of indeno(1,2,3-*cd*)pyrene to the sum of indeno(1,2,3-*cd*)pyrene and benzo[*g*,*h*,*i*]perylene, In/(In + BP), lower than 0.20. A ratio between 0.20 and 0.50 may indicate liquid fossil fuel (vehicle and crude oil) combustion, and a ratio higher than 0.50 suggests grass, wood and coal combustion (Chen et al., 2005a).

Another molecular ratio that has been proposed to differentiate the source of PAHs is fluoranthene to fluoranthene plus pyrene (Fl/Fl + Pyr) with 0.40 being defined as the petroleum/combustion transition point (Yunker et al., 2002). Most petroleum samples have Fl/Fl + Pyr ratio below 0.40 while those of most combustion generated PAHs are above 0.40. In addition, the ratio is further divided into two regions: a ratio between 0.40 and 0.50 is more characteristic of liquid fossil fuel (vehicle and crude oil) combustion whereas a ratio greater than 0.50 is characteristic of grass, wood, or coal combustion (Zhang et al., 2004a).

5.2.4. Fate of PAHs in the atmosphere

Once they enter the atmosphere, PAHs are redistributed between gas and particle phases and are subject to removal mechanisms such as oxidative and photolytic reactions and wet and dry deposition.

5.2.4.1. Atmospheric fallout

Although atmospheric PAHs are partitioned between particulate matter and gas phase, they are mainly associated with particulate matter. PAH concentrations found in the atmosphere are highly dependent on the size of particles, and the highest concentrations are found in inhalable particles.

Kaupp and McLachlan (2000) has investigated the distribution of PAHs within the full size range of atmospheric particles. The study showed that 97% of the PAHs with 5 or more rings, which were all more or less completely particle bound in the atmosphere, were associated with particles with aerodynamic diameters (d_{ae}) $<2.9\,\mu m$. The substance loading decreased steadily with increasing particle size. On average, only 3.4 and 1.2% of the $Cl_{7-8}DD/F$ and the PAHs with 5 or more rings, respectively, were found on large particles with $d_{ae}>8.6\,\mu m$.

As semi-volatile organic compounds, PAHs are transported in the atmosphere as gas and/or particulate phases and scavenged according to various processes: (i) wet deposition: PAHs become associated with rain either by being dissolved in the raindrop or being incorporated as particles; (ii) dry deposition: they are associated with particles, whose transport is complex, depending on various physical factors; (iii) air–water exchange: they may be adsorbed and conversely volatilized when facing large aquatic systems.

Ollivon et al. (2002) has studied atmospheric deposition of PAHs to an urban site in Paris, France. They collected atmospheric fallout to analyze PAHs. The study showed that total PAH concentrations in bulk (dry plus wet) precipitation ranged from 51 to $995\,ng\,l^{-1}$ and were higher than those analyzed in rivers crossing the Paris area. The same trend was observed for PAH concentrations in bulk (gaseous plus particulate) air measured by the Laboratoire d'Hygiene de la Ville de Paris. Monthly fluxes ranged from $5.3\,\mu g m^{-2}$ in August to $63\,\mu g m^{-2}$ in December for total PAHs, with annual flux of $234\,\mu g m^{-2}$, corresponding to 2.1 and $27.7\,\mu g m^{-2}$ for the 6 PAHs of the WHO recommendations and $104\,\mu g m^{-2}$ for a year. The winter loading was two times higher than the summer one, and heating contribution was estimated to be 41% of the annual loading.

Garban et al. (2002) investigated the atmospheric bulk deposition of PAHs onto France. The study showed that atmospheric deposition was the main source of PAHs to terrestrial ecosystems and especially to soils.

5.2.4.2. Photo degradation

The photo degradation of PAHs is a topic of current interest worldwide. Information on the fate of particulate PAHs released to the atmosphere is at present fragmentary and unclear. It is generally assumed, however, that photochemical oxidation processes play an important role. Studies have shown that PAHs associated with atmospheric particulate matter decay rapidly in sunlight under appropriate atmospheric conditions. Their decay rates are strongly influenced by light intensity, temperature, water vapor concentration, and other atmospheric parameters (Kamens et al., 1988). A number of studies have demonstrated that the nature of solid particle surface strongly influences PAHs decay rates. Particle associated organic substances also have important effects on PAH decay (Buulter & Crossley, 1981; McDow et al., 1994; Odum et al., 1994; Jang & McDow, 1995).

Pan et al. (1999) reported detailed observations of PAH decay in aerosols under UV light of 253.7 nm. The study used a high volume sampler to collect the total suspended particles in air with quartz filters as the supporter. The results showed that the photo degradation of PAHs under UV radiation took place immediately, and was a first-order reaction. The photodegradation rate constant (k) is related to the oxidation half-wave potential ($E_{1/2}$) and the structure of the PAHs.

Wang et al. (1997) studied the photochemical behavior of selected PAHs, such as B(a)P, B(k)F and fluoranthene in coal smoke particles, using an indoor Teflon smog chamber. Experiments suggested that the photochemical reaction of PAHs is of first order. The obtained photodegradation rates of PAHs were proportional to light intensity and water vapor concentration. Temperature and PAH loading also influence PAH degradation rates. A model for PAH loss has been developed on the basis of these results and its simulations suggest that coal particle PAH half lives are of the order of a period of days in the winter and a few hours in the summer.

The spectral composition of sunlight reaching the Earth's surface can be characterized by spectral bands, which include the UV-B region (280–315 nm), the UV-A region (315–400 nm), visible light (400–780 nm) and the infrared band (>800 nm). Approximately 4% of the total energy from sunlight reaching the Earth's surface occurs in the UV band. Due to absorption by the stratospheric ozone layer, the minimum wavelength of terrestrial global radiation is approximately 290 nm. Although UV-B radiation contributes less than 1% of the total solar energy reaching the Earth's surface, it may play an important role in the photodegradation of organic pollutants in the environment due to its high photonic energy of approximately 4 eV.

Niu et al. (2004) investigated the photodegradation of PAHs sorbed on the surfaces of spruce (*Picea abies (L.) Karst.*) needles. The role of sunlight and, in particular, the role of short wavelength UV-B radiation was studied in a sun simulator under controlled environmental conditions. The photodegradation of PAHs followed first-order kinetics. No distinct phases of kinetics were observed for the PAHs. Direct photolysis dominated the photodegradation of PAHs.

However, the mechanism of photodegradation is still not well understood. It is suggested that it may be due to the photoreaction of OH free radical striking on the PAH molecules.

5.2.4.3. Reactions with other substances

The PAHs in the atmosphere can react with other substances, and the reaction products can have different toxicity compared with PAHs. For example, PAHs can react with fog, which has NO_X compounds. Their products have direct activity of mutation.

Guo et al. (2000) used the methods of chemical isolation and fluorescence to determine the binding reaction of the PAH fraction in the floating dust of Taiyuan City with DNA. The results showed that the PAH fraction from the floating dust in both day and night were capable of binding with DNA. However, the capacity in the day was stronger than in the night. The PAHs in the floating dust of Taiyuan City can react directly with DNA without being activated or metabolized by organisms. The reaction of PAHs in the day may be further strengthened by the increase in emissions from moving sources and the intensity of sunlight.

PAHs exist in the atmosphere in both vapor- and particulate-phases. PAHs with low molecular weights tend to be more concentrated in the vapor phase while the ones with higher molecular weights are often associated with particulates. Since they are emitted to the atmosphere as a result of incomplete combustion of fossil fuels and other organic materials, a large fraction of them are initially in the gas phase and then sorbed to existing particles. The fate, transport and removal of PAHs from the atmosphere by dry and wet deposition processes are strongly influenced by the gas-particle partitioning of PAHs. Understanding the gas-particle distribution of the PAHs is also helpful in assessing respiratory health effects, since these compounds have been found to be very harmful even at low concentrations. Particle size distributions of PAHs have been studied mostly in Europe and America. Distinct geographical locations and meteorological conditions can result in significant differences in aerosol size distribution. China is unique in many aspects because basic emission control technologies have not been intensively used yet, even though the eastern part of China, including the Pearl River Delta region, has developed quickly economically in the recent two decades.

5.3. PAHs in water and sediments

China has more than 50,000 rivers with catchment areas of some 100 km^2, of which 79 have catchment areas of more than 10,000 km^2. The rivers in China have a total length of 226,800 km and a total flow of more than 2,600,000 million m^3. With the rapid economic development and population increase that have occurred in recent years, the water quality of these rivers and lakes has decreased significantly. Even some drinking water sources are choked by nutriment as well as micropollution of toxic organic compounds. Among the toxic organic compounds existing in the water environment in China, PAHs are important pollutants. Li et al. (2006) reported significant PAH contamination in the middle and lower reaches of the Yellow River, with concentrations of benzo[*a*]pyrene above drinking water standards in most of the stations sampled. Qiao et al. (2006) also found PAH contamination in 25 surface sediment samples collected from Meiliang Bay, Taihu Lake, China, in 2003. Almost all large rivers in China belong to the exterior river system, which directly or indirectly empty into the sea. Therefore, any chemical input from these estuaries may cause unexpected marine environmental problems. Moreover, economy growth and urbanization have accelerated in the last two decades along the Chinese coastline as a result of drastic economic reform initiated in the early 1980s. Yuan et al. (2001) have already detected PAHs in sediment samples collected from three estuaries on the east coast of China from 1994 to 1999. Since sediments are the ultimate sinks and reservoirs of contaminants, it is essential to understand sediment pollution in order to assess the impact of anthropogenic activities on aquatic systems.

Due to their low solubility and hydrophobic nature, PAHs tend to be associated with particulate matter and accumulate in sediment. The contamination of PAHs in water is a complex phenomenon that involves various factors, such as water, suspended particulate matter (SPM) and sediment. Heemken et al. (2000) verified that 80–90% of the PAHs in the total water body is adsorbed to SPM, which emphasizes the importance of measuring particle-bound PAHs. However, the partition equilibrium between water and SPM is not usually available for wild situations due to weather, human activity and other impacts.

In this section, PAH contamination statuses in surface water and sediment were reviewed to gain insight into the possible sources of PAHs and the interaction between different environmental compartments. Additionally, investigations of the PAH homolog profile were conducted to provide useful information on possible pollution sources, and a comparison of PAH patterns in different places in China and abroad were also attempted.

5.3.1. PAH pollution of Yangtze River basins

The Yangtze River (also called Changjiang), the largest river in China, is the third largest river in the world. It is fed by hundreds of tributaries, wanders eastward across the mainland of China, flows through the provinces or autonomous regions of Qinghai, Tibet, Sichuan, Yunnan, Hubei, Hunan, Jiangxi, Anhui, and Jiangsu, and makes an incessant rush into the East China Sea in Shanghai. The Yangtze River has a length of 6300 km and a catchment area of 1.8 million km^2, which equivalent to 1/5 of the total land of China. In recent years, there has been great concern on the effects of increasing inputs of nutrient and organic compounds into the coastal regions of China, and the majority of these surveys focused on coastal seawater and estuarine water. However, few data are available for PAH contamination of the inland waters of China, which usually act as receptors for sewage, industrial effluents, and urban or rural runoff (Tables 5.2 and 5.3).

Zhu et al. (2004) reported the concentrations of 10 PAHs in four bodies of water in Hangzhou, China (July and November 1999–2002). The maximum levels of PAHs in the water bodies (34.4–67.7 $\mu g l^{-1}$) were found in July, while significantly lower PAH concentrations (4.7–15.3 $\mu g l^{-1}$) were measured in November. The measured PAH concentrations in sediments and soils, runoff water, and air particles were 224–4222 ng g^{-1}, 8.3 $\mu g l^{-1}$ and 2.3 $\mu g m^{-3}$, respectively. Clearly, such substantial contamination may lead to acute toxic effects on aquatic organisms. However, the erosion of soil material does not contribute significantly to the contamination of sediments. The atmospheric PAH deposition to water bodies in the city area of Hangzhou was estimated to be 530 tons/a, while the contribution of surface runoff water was

Table 5.2. PAHs concentration in water phase of Yangtze River Basin

Location	Year	ΣPAHs	Average ($\mu g l^{-1}$)	Range ($\mu g l^{-1}$)	Reference
Qiantang River, Hangzhou	July 1999–2002	10	67.70	49.46–71.03	Zhu et al. (2004)
	November 1999–2002		15.31	2.436–46.54	
Inland River, Hangzhou	July 1999–2002		34.43	15.76–58.06	
	November 1999–2002		8.837	1.520–38.71	
West Lake, Hangzhou	July 1999–2002		57.66	38.45–96.21	
	November 1999–2002		9.846	0.989–22.07	
Hangzhou Canal, Hangzhou	July 1999–2002		48.09	21.32–74.44	
	November 1999–2002		4.701	1.104–9.168	
Surface water in Hangzhou	December 2002	10	–	0.989–9.663	Chen et al. (2004)
Minjiang Estuary	November 1999	16	72.4	9.9–474	Zhang et al. (2004b)

Table 5.3. PAHs concentration in sediment of Yangtze River Basin

Location	Year	ΣPAHs	Average level (ng g^{-1} dw l)	Range (ng g^{-1} dw)	Reference
Meiliang Bay, Taihu Lake	2003	16	2563	1207–4754	Qiao et al. (2006)
Qiantang River, Hangzhou	November 2002	10	224.0	139.9–308.0	Zhu et al. (2004)
Inland River, Hangzhou	November 2002	10	674.2	141.4–1560.6	
West Lake, Hangzhou	November 2002	10	664.6	520.2–839.0	
Hangzhou Canal, Hangzhou	November 2002	10	4221.9	2342.2–342.6	
Surface water of Hangzhou	December 2002	10	–	132.7–7343	Chen et al. (2004)
Core sediment in Donghai, Yangtze Estuary	July 1998	7	–	61–7618	Xu et al. (2001)
Core sediment Baoshan, Yangtze Estuary	July 1998	7	–	5–2370	
Core sediment, Yangtze Estuary	September 1996	14	–	80–11,740 (parent PAHs and substituted naphthalene series)	Liu et al. (2000)
Surface sediment, Yangtze Estuary and adjacent East China Sea	–	11	–	22,000–18,2100	Bouloubassi et al. (2001)
Minjiang Estuary	November 1999	16	433	112–877	Zhang et al. (2004b)

estimated to be 30.7 tons/a. The value of PAH input via urban runoff into water was lower than PAH input via atmospheric particle deposition to urban and soil surfaces, suggesting that a great number of PAHs accumulated in soil and urban surfaces. Furthermore, it should be noted that PAH deposition from air to Hangzhou City water bodies was ~10 times larger than that in the Mediterranean Sea (Zhu et al., 2004).

Chen et al. (2004) collected 17 surface water samples and 11 sediment samples of four water bodies, and 3 soil samples near the water-body bank in Hangzhou, China in December 2002. The sum of PAH concentrations ranged from 989 to 9663 $\mu g l^{-1}$ in surface waters, from 132.7 to 7343 $ng\,g^{-1}$ dry wt. in sediments, and from 59.7 to 615.8 $ng\,g^{-1}$ dry wt. in soils. Obviously, the pollution status has not been alleviated compared to the situation in 1999–2002 (Zhu et al., 2004). Similar to the PAH composition of European rivers, 3-ring PAHs dominated in surface waters and soils, while 4-ring PAHs dominated sediments. Furthermore, Chen et al. also evaluated the sources of PAHs in different water bodies by comparing K_{oc} values in sediments of the river downstream with those in soils. PAHs released from industrial wastewater in the past was identified as the source for the PAHs in the Hangzhou section of the Great Canal, while present PAHs in sediment serve as sources of PAHs in surface water. PAHs in the Qiantang River were mostly from soil runoff, while PAHs in the West Lake were from municipal road runoff.

In the middle and lower reaches of the Yangtze River, many large lakes are connected, namely the Dongting Lake, the Poyanghu Lake, the Caohu Lake and the Taihu Lake. According to the GC-MS measurement report of 25 surface sediment samples collected from Meiliang Bay, Taihu Lake, China in 2003, total concentrations of 16 PAHs, identified as priority pollutants by the USEPA, ranged from 1207 to 4754 $ng\,g^{-1}$ dry wt. (Qiao et al., 2006). These PAH levels were higher than those in river sediments in China but were lower than those found in sediments of urban areas and harbors.

Since PAHs are highly hydrophobic, higher level of PAHs are expected in not only sediment but also pore water, possibly due to higher concentrations of dissolved organic carbon or colloids with which the hydrophobic pollutants were strongly associated. Xu et al. analyzed two sediment core samples of ~50 cm long, which were collected from intertidal mud flats at the Baoshan site near a sewage outlet (Shidongkou) and at the Donghai site, the easternmost tidal flat of the Yangtze estuary. The total concentrations of PAHs in the two sediment samples ranged from 61 to 7618 $ng\,g^{-1}$ at the Baoshan site, and from 5 to 2370 $ng\,g^{-1}$ at the Donghai site. Total and individual PAH concentrations in sediment cores were characterized by at least one subsurface maximum, followed by decreased levels both to the surface and with increased depth (Xu et al., 2001). The author explained that this PAH abundance pattern indicated significant petroleum contamination in the Yangtze estuary due to incomplete combustion of fossil hydrocarbons. A few individual PAHs, such as acenaphthalene and anthracene in surface samples of the two cores, are in excess of current sediment quality criteria in the Yangtze estuary, implying significant anthropogenic input. Such PAH levels seem comparable to the published data of the same group in 2000 (Liu et al., 2000), in which the total concentration of PAHs ranged from 80 to 11,740 ng g^{-1}. The historical record of PAHs in the core is found to be in accordance with historical sewage discharge events during the 1980s and 1990s. The distribution of target molecule acenephthene, the fluoranthene/pyrene ratio, the proportion of 2–3- and 4–5-ring PAHs, and the ratio of alkylated naphthalene to parent naphthalene in the core sediments demonstrated that the sources in this area are characterized by petroleum-derived PAH contamination (mainly sewage discharge and the river runoff) and the incorporation of atmospheric inputs. Compared to the core sediment results, PAH contaminations in surface sediments from the Yangtze River estuary, East China Sea, were dominated by biogenic perylene at sampling stations receiving riverine input (Bouloubassi et al., 2001). Bouloubassi et al. found that anthropogenic PAHs released from combustion/pyrolysis processes varied from 17 to 157 ng g^{-1} and fossil PAH level located in 42–187 ng g^{-1}. However, the overall level of anthropogenic PAHs was rather low compared to those of relevant estuaries worldwide.

Compared to that of the main stream of Yangtze River, PAH pollution in some tributaries are more serious. According to the determination profile of 16 priority PAHs in water, pore water, sediment, soil and vegetable samples from the Minjiang River Estuary in China, total PAH concentrations varied from 9.9 to 474 μgl^{-1} in water, 82.1 to 239 μgl^{-1} in pore water, 112 to 877 ng g^{-1} dry wt. in surficial sediments, 128 to 465 ng g^{-1} dry wt. in soil, and 8600 to 111 000 ng g^{-1} dry wt. in Chinese vegetables (Zhang et al., 2004b). PAHs in sediment and soil are comparable to those found in many other similar environments, but the levels of these contaminants in surface water and Chinese vegetables were relatively high compared to data reported elsewhere. Moreover, the concentration gradient implies a potential flux of pollutants from sediment pore water to overlying water. The ratios of selected PAHs indicated that PAHs in the Minjiang River Estuary were mainly derived from incomplete combustion of fossil fuel.

Since toxic contaminants may disturb the biological condition of aquatic ecosystems, toxicological profiles of pollutants in surface water from an area in Taihu Lake, Yangtze Delta, was provided by analyzing genotoxic, hormone disrupting and Ah-receptor activity in water collected in January 1999 at Meiliang Bay, Taihu Lake, China, near the city of Wuxi in the Shanghai area. (Shen et al., 2001). The investigation used an array of in vitro tests, and the results indicated considerable contamination with genotoxic, dioxin-like and hormonal active compounds released into the environment by human activities, to which PAHs might have contributed.

Qiao et al. (2006) indicated that contamination levels of PAHs at most studied sites in Meiliang Bay, except some sites in the northern part of the bay, might not lead to adverse biological effects of the waterbody on the basis of the numerical effect-based sediment quality guideline (SQGs) of the United States. However, the carcinogenic potential of PAH pollution in water should not be neglected. The author used B[*a*]P toxicity equivalents ($TEQs^{carc}$) to express the total PAH levels since there is a good correlation between the benzo[*a*]pyrene level and the total PAH concentration ($r = 0.97$). The average TEQ^{carc} value was $407\,ng\,g^{-1}$ dry wt., and the maximum total TEQ^{carc} value of $856\,ng\,g^{-1}$ dry wt. was found at northern site 22. Compared with those of other sediments of other literature-reported sites, such as the bottom sediments from Guba Pechenga, Barents Sea, Russia (Savinov et al., 2003), $TEQs^{carc}$ values were higher in sediments of Meiliang Bay. Moreover, benzo[*a*]pyrene, a well-known carcinogen, astonishingly accounted for 60% of total TEQ^{carc}.

5.3.2. PAH pollution of Yellow River Basins

The Yellow River rises on the northern slopes of the Bayankela Mountains of Qinghai and traverses nine provinces or autonomous regions including Qinghai, Gansu, Sichuan, Ningxia, Inner Mongolia, Shaanxi, Shanxi, Henan, and Shandong. It is the second largest river in China and falls 4450 m over a length of 5465 km with a drainage area of 795,000 km^2. Similar to the Yangtze River, the Yellow River is a pivotal water supply for northern China and in recent years, has suffered from low water yields and water pollution. Moreover, national petrochemical industrial plants, mines, metallurgy factories and many other pollution sources are located in the middle and lower reaches of the river (Li et al., 1996; Li et al., 2006), and the contamination of PAHs has become one of the major problems in the Yellow River (Gao et al., 2001; Liu et al., 2004; Wang et al., 2004a).

The Yellow River possesses a notable feature that cannot be ignored: it is the largest loess deposit in the world. Because of intense soil erosion, the Yellow River far exceeds any of the world's large rivers in terms of annual sediment transport and is the most turbid large river in the world. Such high suspended-sediment content in water may affect the fate and effect of PAHs in the river to a considerable extent.

Recently, Li et al. (2006) assessed PAH concentrations, distribution between different phases, and transition along the middle and lower reaches of the Yellow River Concentrations of PAHs in water samples from the main stream of Yellow River ranged between 179 and

369 ng l^{-1} for the 15 PAHs with a mean value of 248.2 ng l^{-1}. The relative proportions of the 15 PAHs in all stations of the main stream were similar, and exhibited in the following order: naphthalene (50.5% on average) > phenanthrene (11.4%) > pyrene (7.8%) > fluoranthene (6.3%) > fluorine (6.0%) > dibenzo[*a*,*h*]anthracene (5.1%) > benzo [*g*,*h*,*i*]perylene (2.8%) > indeno[1,2,3-*cd*]pyrene (2.6%) > benzo[*a*]anthracene + chrysene (2.3%) > benzo[*a*]pyrene (1.9%) > benzo[*b*]fluoranthene (1.6%) > benzo[*k*]fluoranthene (1.0%) > anthracene (0.7%). Similar to that of the Yangtze River, the concentration of naphthalene was the highest (137 ng l^{-1}) among the PAHs, possibly because of its popular use in industries and households. Surprisingly, benzo[*a*]pyrene was also detected in high concentrations in main stream of the Yellow River, which exceeded the Environmental Quality Standard for Surface Water of China (2.8 ng l^{-1}, GB3838-2002) in all the stations at the main stream except the one in the Jiaogong Bridge. Like the Yangtze River, PAH concentrations in tributaries were higher than those in the corresponding sites in the main stream. Concentrations of PAHs in the tributaries ranged from 185 to 2182 ng l^{-1} in water for the 15 PAHs, in which the Mengzhou Channel had the highest levels of PAHs, which were almost 10 times higher than that of the main stream. Such a gradient mainly resulted from low water flow and direct wastewater discharge into the channel. However, the author excluded the possibility that PAHs in the main stream of the lower and middle reaches of the Yellow River come from its tributaries because the water flows of the tributaries were not significant enough to cause such pollution. Consequently, the PAHs in the water of the main river of the lower and middle reach of the Yellow River mainly came from the upper reach. The detected concentrations of PAHs in suspended particles were from 54 to 155 mg kg^{-1} dry wt. The relative proportions of the 13 PAHs in all stations of the main river were similar. Just like the situation of the Yangtze River, the proportion of higher molecular weight (5- to 6-ring) PAHs were found to be much higher in suspended particles than that in the water phase. PAH concentrations of suspended particles were mainly correlated with contents of total organic carbon. The average value of total PAHs in sediments from the main stream of Yellow River was 76.8 mg kg^{-1}, among which phenathrene occupied the largest proportion. In contrast to water and suspended particles, the proportions of PAHs in sediment samples from different stations of the main river varied significantly, and PAH levels in sediments were mainly correlated with the volume of particles smaller than 0.01 mm. PAHs in yellow River mainly originated from coal burning, although in some tributaries, PAH inputs could come from the combustion of petroleum (Li et al., 2006).

High sediment load may significantly change the behavior of PAHs in the river. Xia et al. (2006) reported the effect of sediment on biodegradation of chrysene, benzo[*a*]pyrene and benzo[*g*,*h*,*i*]perylene with phenanthrene as a co-metabolite substrate in natural waters from the Yellow River. They found that the biodegradation rates of PAHs increased with the sediment content in the water. Further studies indicated that the enhanced biodegradation rate in the presence of sediment might have been caused by three kinds of mechanisms: sediment enhancement in bacteria population growth, PAHs sorption on the sediment phase described by the dual adsorption–partition model, and the increase in PAH bioavailability by desorption (Xia et al., 2006).

5.3.3. PAH pollution of Pearl River Basins

The Pearl River is one of the largest rivers in the south and among the seven major rivers in China. The river is composed of the West, the North, and the East Rivers and the Pearl River Delta waterway network with a catchment area of 453,700 km^2. Intrigued by the open policy initiated in the early 1980s, the Pearl River Delta has become the most developed region in China in economic terms. The population has increased from 50.6 millions in 1979 to 69.0 millions in 1996, while the gross domestic production in 1997 experienced a 13.5% annual increase in the region compared to an average increase of 7.8% nationwide (Luo et al., 2006). There are many coal, aluminum, tungsten, tin and ferric sulfide mines standing along the waterways in the Pearl River Valley, Commercial/industrial cities such as Guangzhou and Nanning, especially the cities of Shenzhen, Zhuhai, which are listed in the special economic zones, have developed very quickly for the last 20 years that contribute to the boost of the local economy. The industrialization of the areas has resulted in severe environmental problems. Pollution has put the local water environment under very high pressure. Approximately 85% of SPM brought by the Pearl River is deposited in the estuary, and the rest is deposited in the rivers within the Pearl River Delta. Therefore, large amounts of particle-associated contaminants, such as PAHs, generated in the Pearl River Delta may accumulate in the sediments of the estuary and the South China Sea (Luo et al., 2006).

Luo et al. (2004) measured the PAH concentrations in suspended particles and dissolved phase from Baiertang water column and the Macao water column samples collected from the Guangzhou channel of the Pearl River and the Macao harbor. Total PAH concentrations varied from 189 to 637 $ng\,g^{-1}$ in sediments and 422 to 1850 $ng\,g^{-1}$ in SPM. 5,6-ring PAH compounds dominated in sediments and 2,3-ring compounds in SPM samples. While total PAH concentrations varied from 987.1 to 2878.5 ng l^{-1} in the Baiertang water column samples and from 944.0 to 6654.6 ng l^{-1} in the Macao water column samples (Luo et al., 2004). The vertical distribution profiles of pollutants and the partitioning of pollutants between particles and dissolved phases indicate that the pollutants in the water of this region mainly originated from the release and re-suspension of contaminants residing in the sediments. Compared to those of the Jiulong River estuariy and the Minjiang River estuary, the concentrations of PAHs in the Pearl River estuary were relatively higher. Relatively high values of PAHs appeared in sediments, SPM and bivalves at the outlet of the river, waterway and harbor during 1994 and 1997 (Hong et al., 2000). Mai et al. (2003) have made a comprehensive assessment of the input sources and transport pathways of PAHs found in the coastal sediments of Macao, based on measurements of 48 2–7-ring PAHs and 7 sulfur/oxygenated (S/O) PAH derivatives in 45 sediment, 13 street dust, and 68 aerosol samples. Total sediment PAH concentrations ranged from 294 to 12,741 ng g^{-1}, categorized as moderate contamination compared to other regions of Asia and the world. However, the total concentrations of 16 PAHs varied from 4228 to 29,325 ng l^{-1} in water, and from 115 to 1134 ng g^{-1} dry wt. in sediments in samples collected from Daya Bay (Zhou & Maskaoui, 2003). In comparison to many other marine systems studied, the PAH levels in Daya Bay waters were relatively high, and at six sites they were sufficiently high (>10 ng l^{-1}) to cause acute toxicity. The PAH composition pattern in sediments suggest dominance by medium to HMW compounds, and the ratio of certain related PAHs indicate important pyrolytic and petrogenic sources. The author analyzed the distribution coefficient (K_d) of PAHs and indicated that the K_d increased with the particular organic carbon content of the sediments, which is consistent with the PAH partitioning theory. The organic carbon normalized distribution coefficients (K_{oc}) also increased with the compounds' octanol/water partition coefficients (K_{ow}). The concentrations of total polycyclic aromatic hydrocarbons (ΣPAHs) and 15 individual PAH compounds in 20 surface sediments collected from four mangrove swamps in Hong Kong showed that ΣPAH concentrations ranged from 356 to 11,098 ng g^{-1} dry wt. with mean and median values of 1992 and 114.2 ng g^{-1}, respectively. These values were significantly higher than those of marine bottom sediments of Hong Kong harbors, suggesting that mangrove surface sediments accumulate more PAHs. The concentrations of ΣPAHs as well as individual PAH compounds varied significantly among mangrove swamps. The swamps heavily polluted by livestock and industrial sewage, such as Ho Chung and Mai Po, had much higher concentrations of total PAHs and individual PAHs than the other swamps (Tam et al., 2001).

In order to evaluate the risk of PAHs pollution in water to human health, PAHs in sediment and biotic samples including tilapia (*Oreochromis mossambicus*), bighead carp (*Aristichthys nobilis*), grass carp (*Ctenopharyngodon idellus*), crucian carp (*Carassius auratus*) and mandarin fish/fresh water grouper (*Siniperca chuatsi*) collected from different fishponds in the Pearl River Delta (Tanzhou, Sanjiao, Guangzhou, Shipai, Changan and Mai Po) were analyzed (Kong et al., 2005b). Mandarin fish, which belongs to the highest trophic level, accumulated the highest concentrations of PAHs among all fish species. Levels of PAHs in fish samples ranged from 1.91 to 224.03 $\mathrm{ng\,g^{-1}}$ (wet wt.). However, the potency-weighted total concentrations of PAHs in all muscle tissues were below the guideline value of 0.67 $\mathrm{ng\,g^{-1}}$ (wet wt.) for human consumption set by US EPA. In comparison with tilapia fish (*Tilapia mossambicus*) collected from the fishponds in Hong Kong, PAHs concentrations in fish from Pearl River Delta was relatively higher, which indicates that the fishponds in the mainland are more polluted than those in Hong Kong as a result of rapid socioeconomic growth in the region during the past 20 years (Kong et al., 2005a). Because of the bioaccumualation, concentrations of trace organic pollutants in the bivalves were 2–300 times higher than those in the sediments (Hong et al., 2000).

In the assessment of PAH sources, PAH isomer pair ratios were usually used. Ratio values of specific PAH compounds such as Ph/An and Fl/Pyr, were calculated to identify the possible source of PAHs. Values of Fl/Pyr ratio of 1.3–1.7 have been recorded for sediments at remote sites and ca. 1.0 for sites near urban centers (Helfrich & Armstrong, 1986). Values of Ph/An in the range of 3–11 are indicative of urbanized areas, especially of those most impacted by urban runoff, while ratios greater than 11 are indicative of remote sites that are primarily influenced by atmospheric deposition. This may be due to the selective photooxidation of anthracene during long-range transport (Qu et al., 2002). The spatial and temporal variability of PAH pollution in surface sediments and dated core sediments from the Pearl river and estuary in China revealed that the sediments from the sampling stations in the Guangzhou channel have the highest concentrations of PAHs. This may be due to contributions from the large amount of urban/industrial discharges from the city of Guangzhou (Mai et al., 2001). The pyrogenic (combustion) source, characterized by the abundance of parent PAHs, were predominant in the heavily contaminated station near the aging industrial area, and the petrogenic (petroleum-derived) PAHs were more abundant in the stations adjacent to the petrochemical plant and shipping harbor. Biomass and coal combustion are the major PAH sources of the outer part of the Pearl River estuary sediments and that petroleum combustion is the major PAH source of the inner part of estuary sediments (Luo et al., 2006). The SPM samples indicated multiple PAH sources (petroleum, petroleum combustion, and biomass and coal combustion). The distribution of perylene in the SPM samples indicated that the river was the dominant source of perylene in SPM. Compositional analysis and principal component analysis (PCA) suggested that different classes of PAHs in the coastal sediments of Macao might have been derived from different input sources via various transport pathways (Mai et al., 2003). The significant decrease of PAH concentrations in sediments from the Shiziyang channel is mainly attributed to the increasing degradation and desorption of low molecular weight PAHs and alkyl PAHs, and dilution by less contaminated water acid particles from the East river. The PAH contaminants were concentrated on the western side in the Lingding Bay of the Pearl River estuary because of the hydrodynamic and sedimentation conditions. Perylene is a naturally derived PAH. The high concentration of perylene in the sediment was indicative of an in situ biogenic origin. Dating of the sediment cores using Pb-210 indicated that higher PAH concentrations occurred in the sediments deposited after 1980, and higher fluxes of PAHs discharged into the Pearl River were found after 1990. The PAH profiles in four mangrove swamps in Hong Kong showed similar pattern, and were dominated by 2-ring naphthalene, and 3-ring fluorine and phenanthrene (Tam et al., 2001). The mangrove sediments had higher percentages of low molecular weight PAHs. These indicated that PAHs in mangrove sediments might originate from oil or sewage contamination (petrogenic input). Ratio values of Phe/Ant and Flu/Pyr were calculated to evaluate the possible source of PAH contamination in mangrove sediments. These ratios varied among samples, suggesting that mangrove sediments might have a mixed pattern of pyrolytic and petrogenic inputs of PAHs. Sediments collected from Ho Chung mangrove swamp appeared to be more dominated by pyrolytic input while those from Tolo showed strong petrogenic contamination.

5.4. PAHs in soil and plants

5.4.1. Distribution of PAHs in soil

PAHs in soil can be attributed to natural processes and human activities. Individual PAH concentrations in soils produced by natural processes like vegetation fires and volcanic exhalations have been estimated to be in the range of 1–10 $\mu g\,kg^{-1}$. Anthropogenic contribution has greatly affected the soil PAH concentrations. At present, even the lowest measured PAH concentrations in temperate soils are ~10 times higher than the concentrations assumed to have been present prior to industrialization. Generally, PAH concentrations in soil increase with increasing impact of industry, traffic, and domestic heating. PAH concentrations in topsoils increase in the order of arable soils < mineral soils under forest < permanent grassland < urban soils < specifically contaminated sites (Wilcke et al., 2000). The soil system seems to be the important repository for atmospheric PAHs. Once deposited, PAHs can reside for more than 20 years. The accumulation of PAHs in soil may lead to contamination of food chains, and then cause direct or indirect exposure to humans. Moreover, soil PAHs may transport to atmosphere and groundwater through leaching, evaporation and migration. Although soil pollution by PAHs has not been surveyed systematically in China, limited research has revealed the general trends of contamination in the soil of China. Agricultural soil in remote areas is usually uncontaminated. However, suburban and urban soil around big cities like Beijing may contain various kinds of pollutants because of sewage irrigation and air and water discharge of pollutants from industries Cities with PAH concentrations in soil reported in the literature are listed in Table 5.4. A brief scan of the table reveals that PAH concentration in the soil of China varied greatly according to the location and utilities of the sampling site. Generally, urban soil is more heavily contaminated with PAHs than suburban soil. For instance, in Beijing, the PAH concentration is 366–27,825 ng g^{-1} in urban soil while in suburban soil it is less than 7.84 ng g^{-1} (Tang et al., 2005, Ma et al., 2003, 2005a,b). The most heavily contaminated site is the wastewater irrigation area in Shengyang with PAHs content as unbelievably high as 900–27,378 mg kg^{-1} (Song et al., 2005). Because of the number of samples was usually very limited, some of the data may need to be considered with care. The contamination distribution pattern for whole country cannot be built at this stage.

5.4.1.1. PAH contamination in urban soil and suburban soil

Because anthropogenic activities are the main sources of PAHs, the levels of PAHs in soils in urban areas are approximately 2–10 times higher than those in rural areas. An extensive and systematic survey has been undertaken by Tang et al. (2005) to evaluate the PAH contamination of urban soils in Beijing, China. Soil samples were collected from campuses of universities, schools and kindergartens, public squares, fallow land, and roadsides, and were analyzed for 16 PAHs by GC-MS. There was a high variability in the total PAHs (ΣPAHs) concentrations, ranging from less

Table 5.4. PAH concentrations in soil of China

Cities	Sampling site	PAH concentration in soil (ng g^{-1})	No. of samples	Literature
Beijing, urban soils	Campuses of universities, schools and kindergartens, public squares, fallow land, and roadsides	366–27,825		Tang et al. (2005)
Beijing, suburban Soil	Subsoil	n.d.–0.982	45	Ma et al. (2005a)
	Topsoil	0.016–3.884	45	Ma et al. (2005b)
	Greenhouse soil	1.92–7.84		Ma et al. (2003)
Tianjin	Bulk soil	1.08–6.25	2	Tao et al. (2004)
	Rhizosphere	2.25–7.82	2	
	Wastewater irrigated paddy field	3900		Tao et al. (2002)
Hangzhou		59.71–615.8	3	Chen et al. (2004)
Guangzhou	Vegetable land	42–3077	43	Chen et al. (2005a)
Guiyang	Urban	247–1560	8	Hu et al. (2006)
	Suburban	61–511	5	
Xiamen	Jiulong agricultural catchment	0.50–0.95		Maskaoui et al. (2006)
Yangtze Delta Region	Area with copper- and zinc-smelting factory	0–530	65	Xing et al. (2006)
Shenyang	Waste water irrigation area	900,160–2,737,910		Song et al. (2005)

than 366 to 27,825 ng g^{-1}. The highest ΣPAHs concentrations were found at roadsides and industrial sites. Compared to urban soil, suburban soil is much cleaner.

In Guiyang City in Southern China, the total concentration of 16 priority PAHs in the soil of 13 sampling sites varied from 61 to 1560 ng g^{-1} (Hu et al., 2006). Urban samples and suburban samples showed drastically different PAH levels. The concentrations of 16 PAHs for urban soils are at a similar level as those in Beijing—between 247 and 1560 ng g^{-1}—while the concentrations of 16 PAHs for suburban soils are 61–511 ng g^{-1}. In all the samples, PAHs are dominantly composed of 4- and 5-ring species. Three of the samples (sample 8, 12 and 13) have 4-ring PAHs concentrations lower than 5-ring ones, which may be affected by the same pollution source. The other ten samples have 4-ring concentrations higher than 5-ring ones, and they may be affected by other different sources.

5.4.1.2. PAHs in surface soil and subsoil

PAHs usually distribute in different depths of soil, reflecting the source contribution. The concentrations of PAHs frequently increase from the horizon consisting of little decomposed organic material to the lowermost organic horizon, which directly overlays the uppermost mineral soil. The organic material and preferential flow can enhance the transport of organic pollutants in topsoil to the deeper layer. If the upland soil is frequently irrigated or saturated with water for a significant period of the year, the leaching potential of PAHs from the zone of contaminated sites to deeper layers may increase significantly, and the groundwater quality may be endangered. Ma et al. (2005a,b) have carried out a wide survey of PAH contamination in soils in Beijing. Analysis of PAH content in 47 surface soils and 45 pooled subsoil samples collected from the outskirts of Beijing revealed the distribution map of total PAH contents as a contour plot. PAHs in most of the subsoil were lower than those in the topsoil. The concentration range of 16 PAHs in surface soils varied by over two orders of magnitude from 0.016 ng g^{-1} in rural soils to 3.884 ng g^{-1} in suburban soils with the relatively standard deviation of 70.5%. The pollution extent of PAHs at various sampling sites differed greatly. The sum of 17 PAH concentrations varied from not detected to 0.982 ng g^{-1} in subsoil. It was notable that the concentration of BaP in surface soils was 0.005–0.270 ng g^{-1} with a mean of 0.055 ng g^{-1}. The distribution of PAHs in topsoil centered on the HMW PAHs. The 4–6-ring PAHs represented ~66–70% of the total PAHs found in topsoil samples. Source identification of PAHs with the selected marked compounds by PCA and pair ratios of special PAHs (Ph/An vs. Flu/Pyr; ΣCOMB/ΣEPA—PAHs) suggest that pyrogenic origins, especially traffic exhausts, are the dominant sources of PAHs in Beijing outskirt soils. In subsoil, the dominating PAHs were perylene > benzo[*a*]pyrene > benzo[*g,h,i*]perylene > indeno (1,2,3-*cd*)pyrene. The important fact was that the content of 8 carcinogenic PAHs represented 47% of the total priority PAHs among which the concentration of benzo[*a*]pyrene in the subsoil was comparable to that in the topsoil. Analysis of perylene content and the Flu/Pyr ratio shows that the sources of PAHs in the subsoil are combustion and incorporation of the diagenetic PAHs.

5.4.1.3. PAHs in wastewater irrigation field

The water resources in China are distributed unevenly in both space and time, especially in the northern part of China, where sewage and industrial effluents from biological treatment plant have been widely used for agricultural irrigation to compensate for the water shortage. Because of poor control of the wastewater quality and long-term application, pollutant accumulation and relevant ecotoxicological effects may occur, especially for persistent pollutants and permanently bound chemical residues. The total 16 PAHs in a composite sample collected from a wastewater irrigated paddy field near Tianjin was 3.90 mg kg^{-1}, which is ~500 times higher than that in common soils in the same region (Tao et al., 2002). Field surveys for PAH pollution in farmlands irrigated by effluents from biological treatment plants in a suburb of Beijing also showed severe PAH accumulation. Significantly higher concentrations of PAHs were observed in the sampling sites close to the entrance of main wastewater irrigation channels (157–297 ng g^{-1}) in contrast to those along branches (5.14–80.7 ng g^{-1}) and the reference sites (14.8–23.4 ng g^{-1}) (Chen et al., 2005b). Main components of PAHs in these sites were benzo[*b*]fluorathene, benzo [*a*]pyrane, indeno[1,2,3-*cd*]pyrene, dibenzo[*a*,*h*]anthracene and benzo [*g*,*h*,*i*]perylene. Among these PAHs, concentrations of benzo[*a*]pyrane (45.6 ng g^{-1}), indeno[1,2,3-*cd*]pyrene (IcP, 86.3 ng g^{-1}) and benzo[*g*,*h*,*i*] perylene (BgP, 66.9 ng g^{-1}) exceeded the limits of the Netherlands soil quality standard for biodegraded soils. In identification of the sources, the IcP/BgP values of PAHs in soils were closer to that in air particulates from coal/coke source (1.09 + /−0.03 ng g^{-1}). Therefore, both of the PAHs residues in effluents and emission from a nearby coal/coke plant were responsible.

Shenyang is a famous industrial center in northern China. It also has a long history of wastewater irrigation because of its lack of water. Accumulation of PAHs in soil samples collected from seven sites in the upper, middle, and lower reaches along and nearby the wastewater irrigation channel in western Shenyang had unbelievably high concentrations of 900–2738 mg kg^{-1} (Song, et al., 2005). Toxicity effects of contaminated soils on seedling emergence (root length of wheat) and on earthworms mortality and inhibition of body weight showed that the root elongation was inhibited from −20 to 40%, the mortality rates of earthworms ranged from 0 to 40% from the exposure period of two weeks to eight weeks, and earthworm growth rates were inhibited from −19.36 to 34.53%.

5.4.1.4. PAHs in agriculture soil and plants

Crops and vegetables grown in a PAH contaminated agriculture field may uptake the pollutants from the soil causing PAH accumulation in the agriculture products. PAH contamination in agriculture soil and vegetables in Xiamen, Tianjin, and Beijing were reported. The main PAHs found in soil samples were the low molecular weight compounds in Xiamen region (Maskaoui et al., 2006). The total PAHs detected in soil samples ranged from 0.50 to 0.95 ng g^{-1} soil. The highest values of PAHs, which range from 236 to 249 ng g^{-1} soil were detected in the orange tree leaves, showing recent atmospheric inputs of these volatile pollutants. The distribution of PAHs in vegetables were monitored; the concentrations were high and ranged from 8.24 to 58.9 ng g^{-1}. The total concentrations of PAH16 in bulk soil from two sites in Tianjin were 1.08 and 6.25 ng g^{-1}, respectively, with similar patterns (Tao et al., 2004, 2006a). Greenhouses are used widely in agriculture in China. Soils in the greenhouse may also be contaminated by pollutants. The total concentrations of PAHs determined in greenhouse soils from Beijing suburbs were 1.92–7.84 ng g^{-1}. The contamination of PAHs was relatively serious and the most abundant compounds were 4-, 5- and 6-ring unsubstituted PAHs. The profiles reflect the important contributions of traffic on PAHs in greenhouse soils (Ma et al., 2003). The concentrations of PAH16 and individual compounds in the rhizosphere were significantly higher than those in the bulk soil, with mean values of 2.25 and 7.82 ng g^{-1} for the two sites, respectively. Among the eight types of vegetables studied, the highest concentration of PAHs was found in cauliflower. By average, the concentration of PAH16 in the aerial part of vegetables was 6.5 times higher as that in vegetable root, suggesting that foliar uptake is the primary transfer pathway of PAHs from environment to vegetables. Almost all PAH compounds studied were detected in both roots and aerial parts of the vegetables studied. The abundance of higher molecular weight PAHs in vegetables, however, was lower than that in soil. It appears that agricultural soils and vegetables in Tianjin, especially those from the site located immediately next to an urban district and irrigated with wastewater for several decades, were severely contaminated by PAHs (Tao et al., 2004).

PAHs uptaken by plants could be affected by the growing states of the plants and could also be transferred to different parts of the plants. In order to show the relationship of the PAH uptake pathway from the environment, PAHs in cabbages were studied in detail (Tao et al., 2006a). PAH concentrations in cabbages were positively correlated to either gas or particle-bound PAHs in air. A multivariate linear regression with cabbage PAHs as a function of both gas and particle-bound PAHs in air was established to quantitatively characterize the relationship between them. Inclusion of soil PAH concentrations would not improve the model, indicating that the contribution of soil PAHs to cabbage (aerial part) accumulation was insignificant. Investigation of PAH concentrations in various tissues of rice plants sampled from a PAH contaminated site in Tianjin revealed that the levels of PAHs were much higher in roots than in the exposed tissues (Tao et al., 2006b). Grains and internodes accumulated much smaller amounts of PAHs than leaves, hulls or ear axes. No specific gradient trends along roots, stem, ear axes, and grains were observed, suggesting that systematic translocation among them is unlikely. Over the ripening period, PAH concentrations were increased in rice roots and decreased in most above-ground tissues. Significant correlations between PAH and lipid contents can only be observed during full mature stage. The spectra of individual PAH compounds in rice organs including roots were similar to those in air, rather than those in soil. There was also a significant correlation between bioconcentration factor (plant over air) and octanol/air partitioning coefficient (K_{oa}).

5.4.2. Spatial distribution and source of PAHs in soil

The spatial distribution patterns of PAHs in soil are important to regional environmental assessment. Tianjin, a large city located in northern China adjacent to Beijing, has been studied systematically for the spatial distribution and source apportionment of soil PAHs. The city is highly urbanized and industrialized, while a large portion of the surrounding land is used for agriculture. Tianjin contains one main urban district, seven suburban districts and five counties. Soil in the area is heavily contaminated by many kinds of pollutants, including PAHs. Wang, et al. (2003) have studied the spatial structural features of 16 priority PAH compounds in the topsoil of Tianjin area, as well as soil properties. Spherical models with sills could be used to fit all experimental variograms. The spatial structures of PAH contents demonstrated significant anisotropy. Air precipitation caused by the combustion of coal was the key factor in the formation of the spatial structural patterns of PAHs in the topsoil of the Tianjin area. In most cases, PAHs in soils in urban areas of Beijing were found, using the Phe/Ant and Flu/Pyr ratios, to be pyrogenic. These sources included motor vehicle exhausts, industrial activities and coal burning (Tang et al., 2005). Due to the wide variety of emission sources of PAHs and their different tranportation and transformation pathways to soil, commonly used methods for identifying the source of PAHs in the atmosphere, which compare the ratios of concentrations of selected pairs of PAH congeners in the source emissions to the ratios in the contaminated environmental media, may cause great deviation for the source apportionment of PAHs in soil. These ratios can be altered significantly due to differences in the transport of the PAH compounds in a multimedia environment. To examine such changes, a fugacity model was applied to PAH ratios in a model environment (Zhang et al., 2005). The bulk media studied included air, water, soil, and sediment. For air and water, only the solid fractions were considered. The major influences affecting the diagnostic ratio were evaluated, and the uncertainty of the model results was assessed. The model was verified by comparing model calculations with the actual changes in ratio of PAHs as contaminants moved from the sources of the emissions to the surface soil in Tianjin, China. A linear relationship between the rate of emission and the bulk media concentration was identified for each PAH compound in an environmental medium at a steady state and was quantified by a receptor-to-source ratio (R-RS). It was demonstrated that the R-RS values of the two congeners usually differ significantly. Consequentially, PAH ratios changed remarkably from the source emissions to various environmental media. A site-specific rectification factor was defined as the ratio of the two R-RS values of the paired congeners for a specific PAH ratio in a given medium, which can be applied to account for the ratio changes in a multimedia environment. The sensitivity analysis revealed that PAH ratios of the low molecular weight compounds were less stable. The most influential parameters controlling PAH ratios were those pertaining to dry precipitation, surface-to-air diffusion, degradation in air and water, and exchange between water and sediment. The same group of researchers has also used the multivariate spatial analysis in scale-based distribution and source study of PAHs in the topsoil of Tianjin, China (Wang et al., 2006). Data from 188 topsoil samples collected in the Tianjin area were used for the study. The contents of 16 PAHs and soil background properties were determined for all samples. Results show that coal combustion was the major source for the spatial distribution patterns of PAHs in the topsoil of the studied area. It worked mainly at the short-range scale (5–10 km). Significant spatial variation patterns were identified. In contrast, no significant spatial distribution trends at the nugget (0–5 km) or long-range scales (10–50 km) were seen. Long-range transport and site contamination of PAHs might not be key contributors in forming the distribution pattern of PAHs in the topsoil of Tianjin area. Soil organic carbon was one of the important factors that can influence the concentrations of PAHs in soils. It was found that concentrations of ΣPAHs were significantly correlated with that of soil organic carbon (Tang et al., 2005).

The spatial distribution of soil PAHs and the relationship between current soil PAH levels and land use patterns in the Yangtze River Delta in Southeast China were reported by Xing et al. (2006). Many privately owned and so called township enterprises have been established over the last 20 years in rural locations in the Yangtse River Delta, specializing in metal smelting, production of construction materials, and paper manufacturing. Based on a survey for PAHs in surface soils in the area containing 15 small copper- and zinc-smelting furnaces, 65 topsoil (0–20 cm) samples were collected and 16 PAHs were determined. The average total amount of the 16 PAHs ranged from 0 to 530 $\mu g\,kg^{-1}$ (oven dry basis), with a mean concentration of 33.2 $\mu g\,kg^{-1}$. Benzo[*a*]pyrene and indeno[1, 2, 3-*cd*]pyrene were the two main PAHs present at high concentrations, while pyrene and fluorine had very low concentrations. PAH concentrations were higher in uncultivated than in cultivated soils, and areas of woods and shrubbery had the lowest soil PAH contents. The average PAH-homolog concentrations ranked as follows: 5-rings > 3-rings, 4-rings > 6-rings > 2-rings. Much higher concentrations of PAHs were found in the southern part of the sampling area, perhaps due to deposition of airborne particles by the southeasterly winds in the winter and the spring. The author concluded that small smelting furnaces were the dominant source of PAHs that accumulated in the soils, and the southeasterly winds led to the spatial distribution of PAHs in the topsoils. Land vegetation cover and soil utilization patterns also affected the accumulation and distribution of soil PAHs.

In Guiyang city, coal is widely used for industrial and domestic purposes and the number of the vehicle is growing, so PAH contamination from these sources is very important. It was reported that a large proportion of HMW parent PAHs is a typical characteristic of combustion sources and the enrichment of low molecular weight PAHs is common in fresh fuels (Femandes et al., 1997; Baumard et al., 1998). Analysis of PAHs from 13 samples collected in different sites of Guiyang city revealed that PAHs of three samples (8; 12 and 13) may dominantly originate from coal combustion, and PAHs of the other ten samples may dominantly originate from diffusion of traffic exhaust and coal combustion. This opinion is consistent with the details of the three sample sites that are affected by coal combustion sources. The other ten samples are not close to any obvious point source of PAHs and show a feature of 4-ring higher than 5-ring; thus, they may reflect an impact of gaseous diffusion and deposition of mixed PAHs sources, such as traffic exhaust and coal combustion (Hu et al., 2006).

5.4.3. Phase distribution

PAHs are emitted mainly into the atmosphere and have been detected at long distances from their sources. Because of their low vapor pressures, compounds with 5 or more aromatic rings exist mainly adsorbed to airborne particulate matter, such as fly ash and soot. Those with 4 or fewer rings will occur both in the vapor phase and particulate phase. PAHs reach the hydrosphere and pedosphere mainly by dry and wet deposition and road runoff but additionally from industrial wastes containing PAHs and leaching from creosote-impregnated wood. PAHs are adsorbed strongly to the organic fraction of sediments and soils. Sediments and soils are usually considered as the main sinks for PAHs in the environment. In the past 20 years, numerous important studies focused on transport of POPs in multimedia environment (Chiou et al., 1998; Karickhoff et al., 1979), for example, between vapor phase/particle phase in atmosphere, sediment/water, soil/water, biota/water and water/air. It is believed that POP sorption into soil or sediment was dominated by partition into solid organic matter (Chiou et al., 1998; Karickhoff et al., 1979). Small changes of POP mass in the soils/sediments had a major impact on concentrations in 'adjacent' media, such as air or water. The partition coefficients of POPs with soils and sediments (i.e., K_d) are important parameters to characterize the mobility and fate of POPs in soil/sediment–water systems.

To investigate the distribution of PAHs in different environmental media, the concentrations of 10 PAHs in water, sediments, soils, runoff water and atmospheric particles of Hangzhou, China were simultaneously measured five times (July and November 1999–2002) (Zhu et al., 2004). Comparison of PAH levels in sediments and soils led to the conclusion that the erosion of soil material does not contribute significantly to the contamination of sediments. The atmospheric PAH deposition to water bodies in the city area of Hangzhou was estimated to be 530 tons/a, while the contribution of surface runoff water was estimated to be 30.7 tons/a. Analysis of the composition pattern of PAHs by ring size in water, sediment and soil revealed that 3-ring PAHs dominated in surface waters and soils; meanwhile, sediments were mostly dominated by 4-ring PAHs (Chen et al., 2004). The difference pattern of PAH abundance in surface waters, sediments and soils were contributed to two factors. First, water column and soil receives direct PAH inputs from various sources. Second, high molecular mass PAHs undergo sorption in sediment more easily and are resistant to degradation. With the calculated PAH apparent distribution coefficients (K_d) and solid f(oc)-normalized K_d (e.g., $K_{oc} = K_d/\mathrm{f(oc)}$), the sources of PAHs in different water bodies were evaluated by comparison of K_{oc} values in sediments of the river downstream with that in soils. The ratio of K_{oc} of sediment to that of soil is the ratio of PAHs in sediment to that in soil (organic carbon content normalized). In the Qiantang River, the ratio of $K_{oc\ sedi}/K_{oc\ soil}$ and ratio $\mathrm{foc}_{sedi}/\mathrm{foc}_{soil}$ approximate to 1, suggesting that PAHs in Qiantang River were mainly obtained from soil runoff. In the Hangzhou Canal, a $K_{\mathrm{oc\ sedi}}$ larger than K_{oc} (equilibrium partition coefficients of PAHs) and a ratio of $K_{\mathrm{oc\ sedi}}/K_{\mathrm{oc\ soil}}$ much larger than 1 indicated that the Hangzhou Canal was heavily polluted by PAHs released from industrial wastewater in the past years, and now PAHs in sediment may serve as significant sources of PAHs in surface water. In the West Lake, $K_{\mathrm{oc\ sedi}}$ values near the bank is larger than those far from the bank, indicating that municipal road runoff mainly contributed to West Lake PAHs.

Zhang et al. (2004b) studied the levels of 16 priority PAHs in water, pore water, sediment, soil and vegetable samples from Minjiang River Estuary, China. Total PAH concentrations varied from 9.9 to 474 ng l^{-1} in water, 82.1 to 239 ng l^{-1} in pore water, 112 to 877 ng g^{-1} dry wt. in surficial sediments, 128 to 465 ng g^{-1} dry wt. in soil and 8600 to 111 000 ng g^{-1} dry wt. in Chinese vegetables. Overall, the mean concentrations of PAHs were present in higher levels in pore water than those in surface water, due possibly to higher concentrations of dissolved organic carbon or colloids with which the hydrophobic pollutants were strongly associated. Such a concentration gradient implies a potential flux of pollutants from sediment pore water to overlying water. Contamination was dominated by high molecular mass PAH compounds in all samples, indicating combustion-derived sources (e.g., pyrolysis at high temperature). The levels of PAHs in water and vegetables were relatively high in comparison to other studies, although PAHs in sediment and soil were comparable to those found in many other similar environments. The ratios of selected PAHs indicated again that PAHs in Minjiang River Estuary were mainly derived from incomplete combustion of fossil fuel.

5.4.4. Transportation of PAHs in soil

PAHs in soil may partition into soil organic matter (SOM) or adsorb on soil minerals. The sorptive properties of SOM fractions for organic contaminants in soil play an important role on the transportation of PAHs in soil. Xiao et al. (2004) has reported that soil/sediment organic matter can be fractionated into four fractions with a combined wet chemical procedure and that kerogen and black carbon (BC) are major SOM components in soil/sediment samples collected from the industrialized suburban areas of Guangzhou, China. Phenanthrene and naphthalene were used as the sorbates to study PAH's sorption isotherms on four original and four Soxhlet-extracted soil/sediment samples, 15 isolated SOM fractions, and a char as the sorbents. The sorption isotherms of phenanthrene and naphthalene on all the sorbents were variously nonlinear. The particulate kerogen and black carbon (KB) fractions dominated the observed overall sorption by the tested soils and sediments and exhibited more nonlinear sorption with much higher organic carbon-normalized capacities for both sorbates. KB fractions are expected to be the most important soil components affecting bioavailability and the ultimate fate of hydrophobic organic contaminants (HOCs). The isolated KB fractions exhibited much higher sorption capacities than when they were associated with soil/sediment matrixes. It is suggested that a large fraction of the particulate kerogen and BC was not accessible to sorbing HOCs. Encapsulation within soil aggregates and surface coverage by inorganic and organic coatings may have caused large variations in the accessibility of fine kerogen and BC particles to HOCs and hence lowered the sorption capacity of the soil. This variability posts an ultimate challenge for precisely predicting HOC sorption by soils from the contents of different types of SOM. The isolated humic acid exhibited significantly nonlinear sorption, but its contribution to the overall isotherm nonlinearity and sorption capacity of the original soil was insignificant because of its low content in the tested soils and sediments.

Organic matter contents in soils can also influence the accumulation of PAHs in plants. Tao et al. (2006c) have developed a rapid chemical method for determining the bioavailability of PAHs. Four PAHs naphthalene, acenaphthylene, fluorine, and phenanthrene were used to evaluate the extent of bioaccumulation by the roots of wheat plants (Triticum aestivum L.) in soil. The extractabilities of PAHs in the soil were tested by a sequential extraction scheme using accelerated solvent extraction with water, *n*-hexane, and a mixture of dichloromethane and acetone as solvents. The water or *n*-hexane-extractable PAHs were positively correlated to dissolved organic matter (DOM) and negatively correlated to total organic matter (TOM), indicating mobilization and immobilization effects of DOM and TOM on soil PAHs, respectively. The apparent accumulation of PAHs by wheat roots was also positively and negatively correlated to DOM and TOM, respectively. As a result, there were positive correlations between the amounts of PAHs extracted by water or *n*-hexane and the quantities accumulated in plant roots, suggesting the feasibility of using water or *n*-hexanes-extractable fractions as indicators of PAH availability to plants.

5.5. Emission estimation of PAHs in China

In order to evaluate the evolution of PAH contamination in China, it is necessary to estimate their emission. For emission estimation of a pollutant, an emission inventory of a particular activity can be compiled by multiplying the activity rate by the corresponding EF (Xu et al., 2006). The PAH emission sources included (1) industrial coal combustion, including thermoelectric power station and heat plants; (2) domestic coal combustion, including residential and commercial sectors; (3) coke production; (4) nontransport oil combustion; (5) transport oil combustion; (6) straw burning; (7) firewood burning; and (8) primary aluminum production. Source-specific production (aluminum) and consumption (other sources) data for the period 1980–2003 in China were collected from officially published sources. It was estimated that the total emission of PAH16 and total emission of seven carcinogenic PAH components among them (PAH7: BaA, CHR, BbF, BkF, BaP, IcdP and DahA) were 25,300 and 3460 tons, respectively, in China in 2003. Although the emission of PAH16 in 2003 in China was very close to the amount emitted in the United States in 1990 (26,500 tons), the emission of PAH7 from China was much higher than that emitted from the United States in 1990 (2000 tons) or 1996 (1400 tons), respectively. The relatively higher fraction of carcinogenic species in the PAH emission profile in China was closely related to the emission source pattern. The relatively higher portion of HMW species with carcinogenic potential in the emission profile can be attributed to large contributions of domestic coal and coking industry in China. The major sources of PAH emission in China were identified as industrial and domestic coal combustion, coke production, primary aluminum production, transport and nontransport oil combustion, and biomass burning, including straw and firewood. PAH emission profiles were greatly different between China and the other countries, such as the United Kingdom and the United States. In terms of PAH16, biomass burning contributed 60% of the total in China, which is much higher than those in the United Kingdom and the United States. Domestic coal combustion was another important PAH source in China, which contributed 20% of the total and was a unique feature in the emission profile compared with the United States and United Kingdom. The coking industry in China also accounted for a considerable share (16% for PAH16) of the total PAH emission. Compared to the PAH emission from coal consumption, petroleum was not a major contributor. Only 2.2% of the total PAH16 emission was from this source.

Because of the enormous differences in economic development, population density, and size of different provinces in China, total emission, emission density, emission intensity, and emission per capita showed geographical variations. In general, the southeastern provinces were characterized by higher emission density, while those in western and northern China featured higher emission intensity and population-normalized emission. The annual PAH emissions at the provincial level ranged from

253 tons in Sichuan to 0.7 tons in Macao, and the source patterns varied widely. Sichuan contributed the largest portion of PAH emission in China with 79% of the total from biomass burning, which is a typical feature of agricultural provinces. Shanxi ranked second in the emission with a source pattern totally different from that of Sichuan. Shanxi produced 452 million tons of coal and 67 million tons of coke in 2003, accounting for 27 and 38% of those produced in China, respectively. Consequently, the coking industry alone was responsible for 69% of the total PAH emission in the province. Domestic coal combustion was a major PAH source in Beijing and other northern provinces in China, and Qinghai was among a few provinces where aluminum production had a significant contribution to PAH emission. PAH emission density in the southeastern provinces was one order of magnitude higher than that of the other provinces in the west.

China has undergone a rapid population and economic expansion in the last 20 years. With the increase in domestic coal consumption, emission of PAH16 and BaP in China increased 28 and 40%, respectively during the period from 1980 to 1990. As the new round of industrialization and urbanization occurred in the past several years, small and medium size cities and towns with population less than 1 million became the centers of urbanization. Population growth in these agglomerations accounted for over 75% of the total increment in urban population in China. A direct consequence was that domestic coal consumption increased, bringing the PAH emission up again. Increase in coke production was another reason that caused increased PAH emission, particularly the carcinogenic species. The annual production of coke jumped from 122 million tons in 2000 to 178 million tons in 2003, in response to rapidly growing demands both nationally and internationally. It was estimated that coke production would continually increase from 178 million tons in 2003 to 260 million tons in 2005. Obviously, the emission of PAHs from the coke industry will continue to increase rapidly if no measures are taken, either to reduce the production or to reduce the emission during manufacture. Although energy consumption in China went up continuously during the past two decades, annual emission of PAHs fluctuated depending on the amount of domestic coal consumption, coke production, and the efficiency of energy utilization.

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